

The Crystal Structure of Two Polarized Ethylenes

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The structures of 1,1-bis-methylthio-2-*p*-bromobenzoyl-2-cyanoethylene and 1,3-dimethyl-2-[*p*-bromobenzoyl-cyanomethylene]-imidazolidine have been determined by X-ray crystallography.

The length of the carbon-carbon double bond in the first compound, 1.369 Å, indicates only a moderate ground state polarization. The second compound shows a twist of 41° between the imidazolidine and O(1)=C(7)–C(8)–C(12)–N(1) planes, and a C=C bond length of 1.448 Å, indicating a strong steric effect.

The observed bond lengths are discussed in their relation to PPP calculations and experimental rotation barriers.

In recent years several investigators have found by NMR lineshape methods that ethylenes with push-pull substituents (polarized ethylenes) have free energies of activation (ΔG^\ddagger) to rotation around the double bond lower than 25 kcal/mol, in some cases even lower than 6–7 kcal/mol, which is the practical lower limit for most NMR spectrometers (see Ref. 1 for a recent review).

These barriers should be compared to $\Delta H^\ddagger = 62.2$ kcal/mol for 1,2-dideuterioethylene² and 60.0 kcal/mol for *cis*-2-butene.³ It is a popular concept that low torsional barriers are due to low π -bond orders of the bonds concerned. However, this is not necessarily true, since the barriers measure the energy differences between the ground and transition states, whereas the bond order is a function of the electron interaction in the ground state alone. In polarized ethylenes the transition state energy is determined by the capacity of the two parts of the molecule to stabilize respectively a positive and a negative charge. It is therefore of interest to

study the relation between bond lengths and torsional barriers in polarized ethylenes. Some bond lengths resulting from X-ray crystallographic studies of similar compounds have recently been published. The double bond joining the cyclopropene and cyclopentadiene rings in 1,2,3,4-tetrachloro-5,6-dipropylcalicene is 1.37 Å,⁴ and the corresponding bond in 1,2,3,4-tetrachloro-5,6-diphenylcalicene is 1.36 Å.⁵ No torsional barriers are known for these calicenes, but Kende *et al.*⁶ have found barriers in the range 18.0–19.4 kcal/mol for 1-formyl-5,6-dipropylcalicene in different solvents, and Prinzbach⁷ has observed temperature dependent NMR spectra of 1,3-di-*tert*-butyl-5,6-dimethylcalicene, from which free energy barriers of 17.8 kcal/mol (in C₆D₆) and 14.4 kcal/mol (in CCl₄) can be calculated. The exocyclic double bond in 6,6-ethylenedithiofulvene is 1.37 Å,⁸ as compared to 1.346 Å in 6,6-dimethylfulvene, by an electron diffraction study.⁹

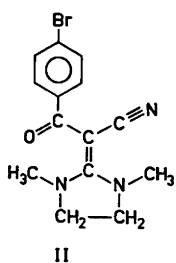
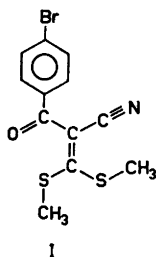
In 2-formyl-6-dimethylaminofulvene the exocyclic double bond is 1.389 Å.¹⁰ The barrier to rotation around this bond could not be measured, probably due to unfavourable conformer distribution, but it is probably lower than the 22.1 kcal/mol barrier found for the simple 6-dimethylaminofulvene.¹¹

More recently, Shmueli *et al.*¹² have studied the crystal structure of 1-dimethylamino-2,2-biscarbomethoxyethylene, for which the length of the double bond was found to be 1.380 Å and the free energy barrier to rotation around this bond 15.6 kcal/mol.

The purpose of the present investigation has been to study the molecular structure of an ethylene with push-pull substituents, for which

the barrier to rotation around the carbon-carbon double bond is known, in order to increase the knowledge of relations between barriers and bond lengths. For this purpose, 1,1-bismethylthio-2-*p*-bromobenzoyl-2-cyanoethylene (TCE) was chosen. The barrier of the bromine-free analogue has been studied by the complete lineshape method, and $\Delta H^\ddagger = 13.8$ kcal/mol, $\Delta S^\ddagger = -17.3$ e.u. and $\Delta G^\ddagger_{300} = 19.0$ kcal/mol were found.¹³ From the rate of rotation at the coalescence temperature and assuming the same entropy of activation, TCE has $\Delta H^\ddagger = 13.9$ kcal/mol and $\Delta G^\ddagger_{300} = 19.1$ kcal/mol.

Furthermore, this study includes the structure of a polarized ethylene, 1,3-dimethyl-2-[*p*-bromobenzoyl-cyanomethylene]-imidazolidine (ICE) (II), for which the NMR spectrum indicates a twisted double bond in solution.¹⁴ The barrier in ICE cannot be studied, but the bromine-free 1,3-dibenzyl analogue has $\Delta G^\ddagger = 9.5$ kcal/mol with the planar state as transition state.



EXPERIMENTAL

The preparation of TCE¹⁵ and the bromine-free analogue of ICE¹⁶ has been described previously. ICE was prepared similarly and was obtained in 82% yield as pale yellow prisms, m.p. 183.5–185 °C after recrystallization from toluene. (Found: C 52.5; H 4.36; Br 25.1; N 13.1; O 4.94. $C_{14}H_{14}BrN_3O$ (320.19) requires C 52.5; H 4.41; Br 25.0; N 13.1; O 5.00).

X-Ray single crystal data for the two compounds were collected on a Picker FACS I automatic diffractometer using graphite monochromated $CuK\alpha$ radiation. Reflexions up to $2\theta = 124^\circ$ were measured with a 2.0 degree $\theta - 2\theta$ scan. The scanning speed was 1 degree min^{-1} . The background level was determined from 10 second counts on each side of the reflexion.

Lorentz and polarization factors were applied, but no correction was made for extinction or absorption. Atomic scattering factors were taken from the International Tables for X-Ray

Crystallography¹⁷ except for hydrogen in which case the values of Stewart, Davidson and Simpson¹⁸ were used. All calculations were performed on a Datsaab D21 – PDP15 dual computer system with programs developed at the Crystallography Group.

CRYSTAL DATA

TCE	$C_{12}H_{10}BrNOS_2$
M =	328.25
Unit cell:	$a = 7.97, b = 13.00, c = 6.53 \text{ \AA}$
	$\beta = 102.19^\circ$
V =	661.28 \AA^3
Z =	2
D_c =	1.648 $g\text{ cm}^{-3}$
D_m =	1.658 $g\text{ cm}^{-3}$
Absent reflexions:	0 <i>k</i> 0 for <i>k</i> odd
Spacegroup	$P2_1$

ICE	$C_{14}H_{14}BrN_3O$
M =	320.22
Unit cell:	$a = 9.07, b = 11.81,$
	$c = 13.45 \text{ \AA}$
	$\beta = 105.08^\circ$
V =	1.391.16 \AA^3
Z =	4
D_c =	1.529 $g\text{ cm}^{-3}$
D_m =	1.525 $g\text{ cm}^{-3}$
Absent reflexions:	$h0l$ for <i>l</i> odd, 0 <i>k</i> 0 for <i>k</i> odd
Spacegroup	$P2_1/c$

STRUCTURE DETERMINATION AND REFINEMENT

TCE. In total 1177 independent reflexions were measured of which 1164 were more than two standard deviations above background and used in the structure analysis. The non-hydrogen atom positions were found from successive electron density series starting with the phases of the bromine atom. The hydrogen atoms were included at their expected positions which were compatible with the peaks in a difference synthesis. In the final least-squares treatment using the full matrix all positional parameters were refined. Anisotropic temperature factors were used except for the hydrogen atoms which were given isotropic temperature factors corresponding to those of their parent atoms. The *B*-values were not refined. At an *R*-value of 0.037 no further improvement occurred and the refinement was terminated.

Table 1. Fractional positional coordinates in TCE and temperature factors for the hydrogen atoms. The standard deviations (within brackets) are multiplied by 10^4 and 10^3 for the hydrogen atoms.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	$B(\text{\AA}^2)$
Br(1)	0.9529	(0.6)	0.4996	(0)	-0.2351	(0.8)	
S(1)	0.1803	(1)	0.7363	(1)	0.5303	(2)	
S(2)	0.4384	(2)	0.8835	(1)	0.7481	(2)	
O(1)	0.3001	(5)	0.6385	(4)	0.2293	(7)	
N(1)	0.7309	(6)	0.8869	(4)	0.3724	(8)	
C(1)	0.7984	(6)	0.5583	(4)	-0.0852	(8)	
C(2)	0.8606	(6)	0.5972	(4)	0.1153	(8)	
C(3)	0.7480	(7)	0.6414	(4)	0.2232	(8)	
C(4)	0.5707	(6)	0.6421	(4)	0.1384	(8)	
C(5)	0.5078	(6)	0.5997	(4)	-0.0594	(8)	
C(6)	0.6204	(6)	0.5593	(3)	-0.1721	(8)	
C(7)	0.4405	(6)	0.6796	(4)	0.2582	(7)	
C(8)	0.4838	(6)	0.7656	(3)	0.4122	(7)	
C(9)	0.3810	(6)	0.7912	(3)	0.5487	(7)	
C(10)	0.1026	(8)	0.7863	(7)	0.7492	(11)	
C(11)	0.6666	(8)	0.8762	(5)	0.8339	(9)	
C(12)	0.6239	(6)	0.8316	(4)	0.3942	(7)	
H(21)	0.969	(9)	0.592	(5)	0.159	(9)	2.91
H(31)	0.788	(8)	0.666	(5)	0.346	(10)	2.61
H(51)	0.387	(7)	0.598	(5)	-0.112	(9)	2.44
H(61)	0.579	(7)	0.541	(5)	-0.347	(9)	2.58
H(101)	0.062	(9)	0.860	(8)	0.700	(11)	4.02
H(102)	0.171	(10)	0.784	(6)	0.885	(13)	4.02
H(103)	-0.032	(8)	0.764	(7)	0.734	(11)	4.02
H(111)	0.725	(9)	0.908	(5)	0.760	(11)	3.06
H(112)	0.702	(8)	0.813	(6)	0.829	(11)	3.06
H(113)	0.747	(8)	0.919	(5)	0.924	(11)	3.06

Table 2. Anisotropic thermal parameters for the non-hydrogen atoms of TCE in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$. The standard deviations (within brackets) have been multiplied by 10^4 .

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Br(1)	0.0394(4)	0.0581(4)	0.0490(4)	-0.0156(3)	0.0190(3)	0.0073(2)
S(1)	0.0197(6)	0.0490(7)	0.0444(7)	-0.0049(6)	0.0118(5)	-0.0030(5)
S(2)	0.0286(7)	0.0515(8)	0.0491(8)	-0.0228(6)	0.0129(6)	-0.0012(5)
O(1)	0.0245(19)	0.0630(24)	0.0575(26)	-0.0290(22)	0.0150(18)	-0.0133(18)
N(1)	0.0436(26)	0.0535(26)	0.0425(23)	-0.0092(22)	0.0196(22)	-0.0214(23)
C(1)	0.0302(23)	0.0356(25)	0.0388(25)	-0.0094(22)	0.0102(20)	0.0038(18)
C(2)	0.0241(24)	0.0460(25)	0.0410(27)	-0.0117(23)	0.0062(20)	0.0043(21)
C(3)	0.0264(22)	0.0420(24)	0.0302(23)	-0.0120(21)	0.0022(19)	0.0023(20)
C(4)	0.0240(22)	0.0327(23)	0.0308(22)	0.0041(19)	0.0014(19)	0.0018(18)
C(5)	0.0210(22)	0.0393(22)	0.0351(23)	0.0002(19)	0.0022(20)	0.0011(18)
C(6)	0.0332(26)	0.0346(23)	0.0310(24)	-0.0023(18)	0.0059(20)	-0.0024(18)
C(7)	0.0313(27)	0.0341(25)	0.0269(25)	-0.0002(16)	0.0042(22)	0.0015(17)
C(8)	0.0208(20)	0.0342(22)	0.0302(19)	-0.0009(18)	0.0119(17)	0.0013(16)
C(9)	0.0211(19)	0.0316(19)	0.0307(22)	0.0019(19)	-0.0016(17)	0.0016(17)
C(10)	0.0350(29)	0.0801(43)	0.0470(35)	-0.0126(32)	0.0218(25)	0.0059(31)
C(11)	0.0342(28)	0.0544(33)	0.0325(24)	-0.0111(25)	0.0116(21)	-0.0031(22)
C(12)	0.0278(25)	0.0378(22)	0.0288(23)	-0.0058(19)	0.0123(19)	-0.0038(22)

Table 3. Fractional positional parameters for the atoms of ICE and isotropic temperature factors for the hydrogen atoms. The standard deviations (within brackets) are multiplied by 10^4 .

	<i>x</i>	$\sigma(x)$	<i>y</i>	$\sigma(y)$	<i>z</i>	$\sigma(z)$	<i>B</i> (Å ²)
Br(1)	0.0143	(0.6)	0.3661	(0.5)	-0.4018	(0.3)	
O(1)	0.4599	(3)	0.2248	(2)	0.0692	(2)	
N(1)	0.2380	(4)	0.5849	(3)	0.0780	(2)	
N(2)	0.6454	(4)	0.3644	(2)	0.2444	(2)	
N(3)	0.4680	(4)	0.4366	(3)	0.3086	(2)	
C(1)	0.1286	(4)	0.3533	(3)	-0.2620	(2)	
C(2)	0.2852	(4)	0.3384	(3)	-0.2404	(2)	
C(3)	0.3665	(4)	0.3277	(3)	-0.1391	(2)	
C(4)	0.2942	(4)	0.3343	(3)	-0.0596	(2)	
C(5)	0.1382	(4)	0.3515	(3)	-0.0833	(3)	
C(6)	0.0541	(4)	0.3601	(3)	-0.1850	(3)	
C(7)	0.3916	(4)	0.3158	(3)	0.0491	(2)	
C(8)	0.3992	(4)	0.4049	(3)	0.1215	(2)	
C(9)	0.5023	(4)	0.4003	(3)	0.2236	(2)	
C(10)	0.7355	(5)	0.3461	(4)	0.1717	(3)	
C(11)	0.3188	(5)	0.4647	(4)	0.3211	(3)	
C(12)	0.3087	(4)	0.5031	(3)	0.0966	(2)	
C(13)	0.7187	(5)	0.3712	(3)	0.3556	(3)	
C(14)	0.6013	(5)	0.4310	(3)	0.3985	(3)	
H(21)	0.343		0.336		-0.302		3.25
H(31)	0.492		0.314		-0.120		3.21
H(51)	0.083		0.358		-0.021		3.52
H(61)	-0.067		0.374		-0.204		3.88
H(101)	0.798		0.265		0.188		4.24
H(102)	0.820		0.414		0.178		4.24
H(103)	0.663		0.344		0.094		4.24
H(111)	0.325		0.548		0.357		4.73
H(112)	0.288		0.402		0.371		4.73
H(113)	0.238		0.465		0.246		4.73
H(131)	0.746		0.287		0.390		4.05
H(132)	0.827		0.420		0.372		4.05
H(141)	0.639		0.515		0.427		3.74
H(142)	0.574		0.382		0.460		3.74

The weight assigned to each observation in the refinement¹⁹ was

$$w = 1 + [(|F_o| - 1.67|F_{\min}|)/1.67|F_{\min}|]^2$$

Corrections for anomalous dispersion were applied for bromine and sulfur.

ICE. The intensities of 2442 reflexions were recorded of which 2127 were more than 2σ above background and used in the analysis. The structure determination procedure was analogous to that for TCE except that it was not possible to refine the hydrogen positions. The final *R*-value was 0.043. The weighting scheme used was

$$w = 1 + [(|F_o| - 10.4|F_{\min}|)/15.5|F_{\min}|]^2$$

DISCUSSION

The final atomic parameters are given in Tables 1-4. Structure factor lists can be obtained on request from the Crystallography Group. Distances and angles are given in Figs. 1 and 2 which also show the atomic numbering and in Tables 5 and 6 where the standard deviations are included. Least-squares planes through various parts of the molecules are given in Tables 7 and 8. Stereoscopic pairs of the molecules are shown in Figs. 3 and 4.

The dimensions of the two bromobenzene groups are normal. The mean value of the C-C bond is 1.388 Å in TCE and 1.384 Å in ICE. The average angle is 120.0° in both structures. In both cases C(7) is about 0.1 Å out of

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of ICE in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$. The standard deviations (within brackets) have been multiplied by 10^4 .

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Br(1)	0.0702(3)	0.1003(4)	0.0303(2)	0.0021(2)	-0.0025(2)	-0.0129(3)
O(1)	0.0634(16)	0.0411(13)	0.0346(12)	-0.0012(10)	0.0114(12)	0.0122(12)
N(1)	0.0617(20)	0.0503(18)	0.0489(18)	-0.0008(14)	0.0142(16)	0.0126(16)
N(2)	0.0518(18)	0.0513(17)	0.0306(14)	0.0023(12)	0.0039(13)	0.0055(15)
N(3)	0.0669(20)	0.0518(18)	0.0253(14)	-0.0061(12)	0.0109(14)	0.0000(16)
C(1)	0.0530(21)	0.0489(20)	0.0284(16)	-0.0004(14)	0.0039(15)	-0.0076(17)
C(2)	0.0549(21)	0.0472(20)	0.0303(17)	-0.0020(14)	0.0157(16)	-0.0019(17)
C(3)	0.0501(20)	0.0422(18)	0.0320(16)	-0.0015(13)	0.0140(15)	0.0002(16)
C(4)	0.0472(19)	0.0380(17)	0.0266(15)	-0.0014(12)	0.0093(14)	0.0003(15)
C(5)	0.0449(19)	0.0600(22)	0.0332(17)	-0.0046(15)	0.0140(15)	-0.0023(17)
C(6)	0.0456(20)	0.0612(23)	0.0412(19)	-0.0046(16)	0.0099(16)	-0.0009(18)
C(7)	0.0466(19)	0.0430(18)	0.0264(15)	-0.0009(13)	0.0127(14)	-0.0002(16)
C(8)	0.0473(19)	0.0396(17)	0.0260(15)	-0.0007(13)	0.0090(14)	0.0060(15)
C(9)	0.0543(20)	0.0347(17)	0.0271(15)	0.0019(12)	0.0095(15)	0.0010(15)
C(10)	0.0498(22)	0.0705(26)	0.0501(22)	0.0017(19)	0.0125(18)	0.0049(20)
C(11)	0.0799(29)	0.0670(25)	0.0420(20)	-0.0032(18)	0.0283(20)	0.0142(23)
C(12)	0.0489(19)	0.0469(19)	0.0284(16)	-0.0033(14)	0.0108(14)	0.0005(16)
C(13)	0.0709(26)	0.0540(22)	0.0341(18)	0.0040(16)	-0.0058(18)	-0.0055(20)
C(14)	0.0803(28)	0.0541(22)	0.0275(16)	0.0002(15)	0.0027(18)	-0.0108(21)

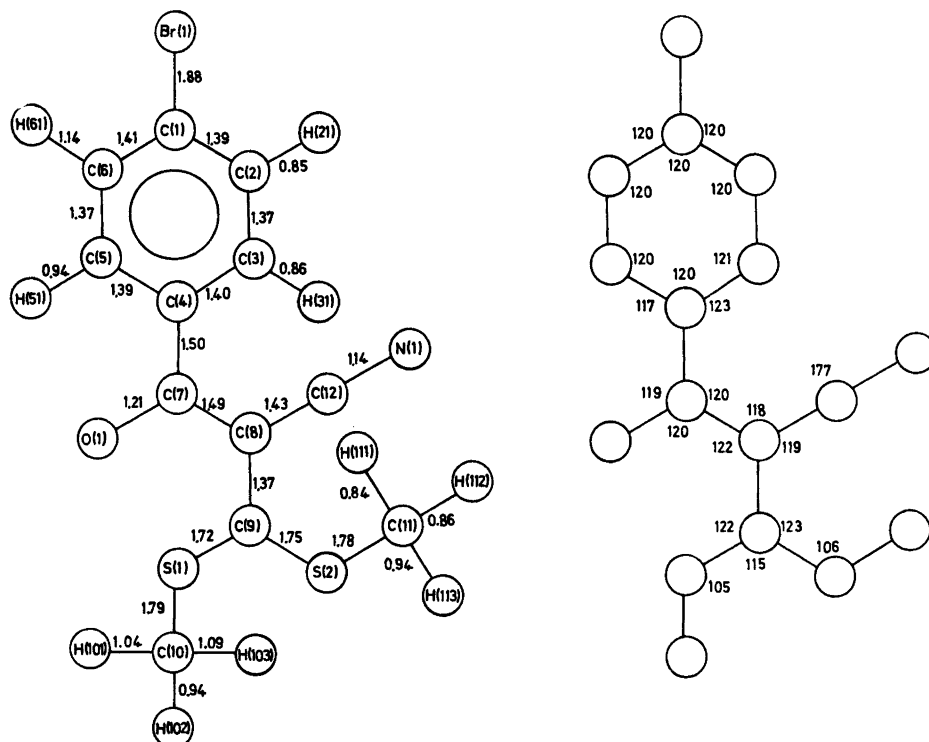


Fig. 1. Bond distances and angles in TCE.

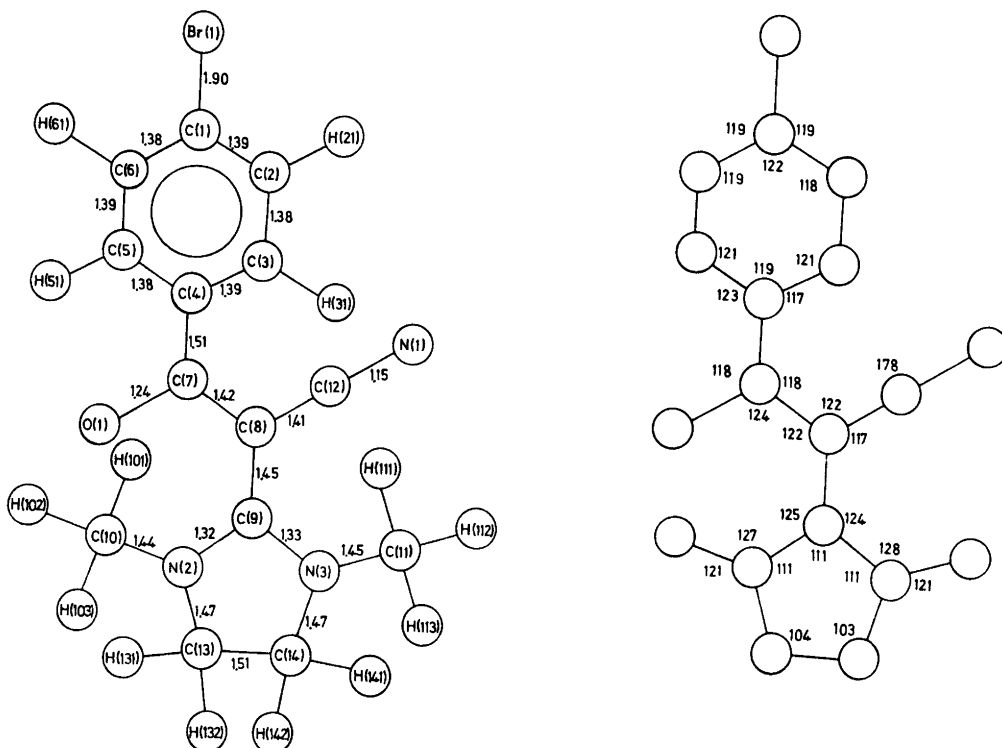


Fig. 2. Bond distances and angles in ICE.

the plane of the ring at the same time as the carbonyl group is twisted 32.1° (TCE) and 60.7° (ICE) from the plane. Whereas in ICE O(1) is near the plane through C(7), C(8) and C(12), it is 0.35 \AA off the corresponding plane in TCE. The calculated twist [angle between planes through C(7), C(8), C(12) and C(9), N(2), N(3) and C(9), S(1), S(2) respectively] around the double bond is 15.2° in TCE and 41.1° in ICE. In TCE most of the effect appears to be due to the change in direction of the C(9)–S(1) bond.

The double bond in ethylene is given lengths between 1.332 and 1.339 \AA .²⁰ Using 1.337 \AA for this bond, and 1.517 \AA for a C(sp^2)–C(sp^2) bond with zero π -bond order and zero rotational barrier,²¹ direct proportionality between barriers and bond orders (and a linear relation (4) between bond orders and bond lengths) should have given a C(8)–C(9) bond length of 1.477 \AA . The experimental value for this bond, 1.369 \AA , shows that no barrier-bond order proportionality exists. To obtain a general idea of electron distribution and bond lengths in TCE, calcula-

tions have been performed by the PPP method modified according to Roos and Skancke.²² The modified matrix elements are given by (1) and (2), where ν refers to atoms directly bonded to μ , and λ to all atoms except μ . Alkyl groups were not taken into account.

$$F_{\mu\mu} = H_{\mu\mu}^{\text{core}} - 1/2q_{\mu}\gamma_{\mu\mu} + \sum_{\lambda \neq \mu} q_{\lambda}\gamma_{\mu\lambda} \quad (1a)$$

$$H_{\mu\mu}^{\text{core}} = W_{\mu\mu} - (n_{\mu} - 1)\gamma_{\mu\mu} - \sum_{\lambda \neq \mu} n_{\lambda}\gamma_{\mu\lambda} \quad (1b)$$

$$W_{\mu\mu} = W_{\mu\mu}^{\circ} + \sum_{\nu} \Delta W_{\mu\nu} \quad (1c)$$

$$\Delta W_{\mu\nu} = \Delta W_{\mu\nu}^{\circ} + \delta_{\mu\nu}^W (R_{\mu\nu} - R_0) \quad (1d)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2}p_{\mu\nu}\gamma_{\mu\nu} \quad (2a)$$

$$\beta_{\mu\nu} = \beta_{\mu\nu}^{\circ} + \delta_{\mu\nu}^{\beta} (R_{\mu\nu} - R_0) \quad (2b)$$

Repulsion integrals between nearest neighbours are given by (3). Other two-centre repulsion integrals are calculated by the

$$\gamma_{\mu\lambda} = \gamma_{\mu\lambda}^{\circ} + \delta_{\mu\lambda}^{\gamma} (R_{\mu\nu} - R_0) \quad (3)$$

Table 5. Interatomic distances (Å) and angles (°) (TCE), with e.s.d.'s.

Br(1)–C(1)	1.882(0.006)
S(1)–C(9)	1.724(0.005)
–C(10)	1.790(0.008)
S(2)–C(9)	1.752(0.005)
–C(11)	1.779(0.006)
O(1)–C(7)	1.212(0.006)
N(1)–C(12)	1.142(0.007)
C(1)–C(2)	1.388(0.007)
–C(6)	1.405(0.007)
C(2)–C(3)	1.374(0.008)
C(3)–C(4)	1.396(0.007)
C(4)–C(5)	1.391(0.007)
–C(7)	1.502(0.007)
C(5)–C(6)	1.374(0.008)
C(7)–C(8)	1.490(0.007)
C(8)–C(9)	1.369(0.007)
–C(12)	1.427(0.007)
C(2)–H(21)	0.85 (0.07)
C(3)–H(31)	0.86 (0.06)
C(5)–H(51)	0.94 (0.06)
C(6)–H(61)	1.14 (0.06)
C(10)–H(101)	1.04 (0.10)
–H(102)	0.94 (0.08)
–H(103)	1.09 (0.07)
C(11)–H(111)	0.84 (0.08)
–H(112)	0.86 (0.08)
–H(113)	0.94 (0.06)
C(9)–S(1)–C(10)	105.4 (0.3)
C(9)–S(2)–C(11)	106.4 (0.3)
Br(1)–C(1)–C(2)	119.6 (0.4)
–C(6)	120.3 (0.4)
C(2)–C(1)–C(6)	120.0 (0.5)
C(1)–C(2)–C(3)	119.5 (0.4)
C(2)–C(3)–C(4)	120.7 (0.5)
C(3)–C(4)–C(7)	122.8 (0.4)
–C(5)	119.7 (0.5)
C(5)–C(4)–C(7)	117.3 (0.4)
C(4)–C(5)–C(6)	119.9 (0.4)
C(1)–C(6)–C(5)	120.0 (0.4)
C(4)–C(7)–O(1)	119.2 (0.5)
O(1)–C(7)–C(8)	120.4 (0.5)
C(4)–C(7)–C(8)	120.4 (0.4)
C(7)–C(8)–C(9)	122.3 (0.4)
–C(12)	117.8 (0.4)
C(9)–C(8)–C(12)	119.3 (0.4)
C(8)–C(9)–S(1)	121.6 (0.3)
–S(2)	123.4 (0.4)
S(1)–C(9)–S(2)	115.0 (0.3)
C(8)–C(12)–N(1)	176.7 (0.5)

Table 6. Interatomic distances (Å) and angles (°) (ICE) with e.s.d.'s.

Br(1)–C(1)	1.902(0.003)
O(1)–C(7)	1.235(0.004)
N(1)–C(12)	1.151(0.005)
N(2)–C(9)	1.324(0.005)
–C(10)	1.444(0.006)
–C(13)	1.473(0.004)
N(3)–C(9)	1.332(0.005)
–C(11)	1.445(0.006)
–C(14)	1.472(0.004)
C(1)–C(2)	1.385(0.005)
–C(6)	1.378(0.006)
C(2)–C(3)	1.377(0.004)
C(3)–C(4)	1.394(0.005)
C(4)–C(5)	1.382(0.005)
–C(7)	1.514(0.004)
C(5)–C(6)	1.385(0.005)
C(7)–C(8)	1.423(0.004)
C(8)–C(9)	1.448(0.004)
–C(12)	1.410(0.005)
C(13)–C(14)	1.512(0.006)
C(9)–N(2)–C(10)	126.9 (0.3)
–C(13)	110.8 (0.3)
C(10)–N(2)–C(13)	120.7 (0.3)
C(9)–N(3)–C(11)	127.5 (0.3)
–C(14)	111.4 (0.3)
C(11)–N(3)–C(14)	120.6 (0.3)
Br(1)–C(1)–C(2)	118.9 (0.3)
–C(6)	119.4 (0.3)
C(2)–C(1)–C(6)	121.8 (0.3)
C(1)–C(2)–C(3)	118.4 (0.4)
C(2)–C(3)–C(4)	121.1 (0.3)
C(3)–C(4)–C(5)	119.2 (0.3)
–C(7)	117.4 (0.3)
C(5)–C(4)–C(7)	123.3 (0.3)
C(4)–C(5)–C(6)	120.5 (0.4)
C(1)–C(6)–C(5)	119.1 (0.3)
O(1)–C(7)–C(4)	118.0 (0.3)
–C(8)	124.2 (0.3)
C(4)–C(7)–C(8)	117.8 (0.3)
C(7)–C(8)–C(9)	121.7 (0.3)
–C(12)	121.7 (0.3)
C(9)–C(8)–C(12)	116.6 (0.3)
N(2)–C(9)–N(3)	110.9 (0.3)
–C(8)	124.6 (0.3)
N(3)–C(9)–C(8)	124.4 (0.3)
N(1)–C(12)–C(8)	178.2 (0.3)
N(2)–C(13)–C(14)	103.7 (0.3)
N(3)–C(14)–C(13)	102.5 (0.3)

hard sphere approximation of Parr.²³ The parameters W_0 , ΔW_0 , β_0 , and the different δ values are taken from the work of the Stockholm School and are collected together with the pertinent references in Table 9. The cyano group has not been parametrized, and instead the parameters for pyridine nitrogen have been employed here. The bond lengths were calcu-

lated by an iterative procedure according to Sundbom.²⁴ An idealized geometry was used in the first calculations, assuming a planar molecule with single and double bond lengths taken from similar systems. The imidazolidine ring in ICE was regarded as a regular pentagon, and all other bond angles were assumed to be 120°. Using the π -bond orders from the first calcula-

Table 7. Some least-squares planes in TCE. Equations referred to the crystal axes.

Planes	Equations			
(a) C(1) C(2) C(3) C(4) C(5) C(6)	$0.12315X + 0.96337Y - 0.23824Z - 0.65558 = 0.$			
(b) O(1) C(7) C(8)	$0.16576X - 0.88006Y + 0.44500Z + 0.41017 = 0.$			
(c) C(7) C(8) C(12)	$0.43592X - 0.83236Y + 0.34227Z + 0.28528 = 0.$			
(d) S(1) S(2) C(9)	$0.21557X - 0.90845Y + 0.35812Z + 0.44015 = 0.$			
Deviations from the planes (Å)				
	(a)	(b)	(c)	(d)
Br(1)	-0.011			
S(1)			-0.630	0.000 ^a
S(2)			-0.027	0.000 ^a
O(1)	-0.698	0.000 ^a	-0.345	0.071
N(1)		-0.811	-0.064	-0.765
C(1)	0.010 ^a			
C(2)	-0.022 ^a			
C(3)	0.015 ^a	0.671		
C(4)	0.003 ^a	0.013	0.439	
C(5)	-0.015 ^a	-0.581		
C(6)	0.008 ^a			
C(7)	-0.098	0.000 ^a	0.000 ^a	0.105
C(8)	0.521	0.000 ^a	0.000 ^a	-0.035
C(9)		0.206	-0.181	0.000 ^a
C(10)			-0.635	0.167
C(11)			1.232	0.887
C(12)		-0.416	0.000 ^a	-0.406

^a Atoms defining plane.

Table 8. Some least-squares planes in ICE. Equations referred to the crystal axes.

Planes	Equations			
(a) C(1) C(2) C(3) C(4) C(5) C(6)	$0.10132X + 0.99479Y + 0.01116Z - 0.36201 = 0.$			
(b) O(1) C(7) C(8)	$0.71008X + 0.40629Y - 0.57507Z - 0.37812 = 0.$			
(c) C(7) C(8) C(12)	$0.65095X + 0.44419Y - 0.61559Z - 0.36494 = 0.$			
(d) N(2) N(3) C(9) C(13) C(14)	$0.28933X + 0.90832Y - 0.30206Z - 0.44137 = 0.$			
Deviations from the planes (Å)				
	(a)	(b)	(c)	(d)
Br(1)	-0.010			
O(1)	-1.071	0.000 ^a	-0.097	
N(1)		-0.185	0.021	
N(2)		0.990	0.777	0.031 ^a
N(3)		-0.518	-0.657	-0.030 ^a
C(1)	-0.005 ^a			
C(2)	0.010 ^a			
C(3)	-0.005 ^a	1.075		
C(4)	-0.004 ^a	0.010	0.137	
C(5)	0.009 ^a	-1.007		
C(6)	-0.004 ^a			
C(7)	-0.090	0.000 ^a	0.000 ^a	-0.664
C(8)	0.971	0.000 ^a	0.000 ^a	0.062
C(9)		0.142	0.026	0.000 ^a
C(10)				0.402
C(11)				-0.284
C(12)		-0.114	0.000 ^a	0.896
C(13)				-0.044 ^a
C(14)				0.044 ^a

^a Atoms defining plane.

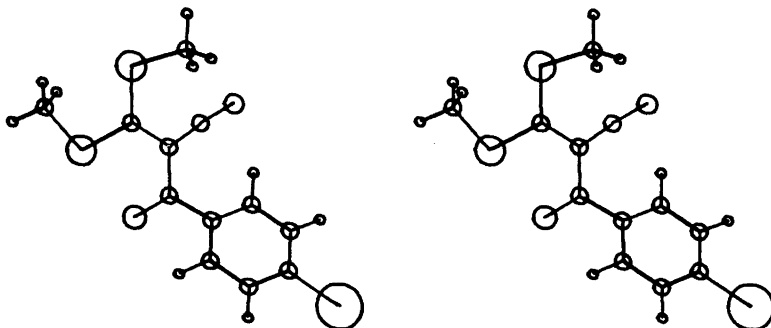


Fig. 3. Stereoscopic pair of TCE.

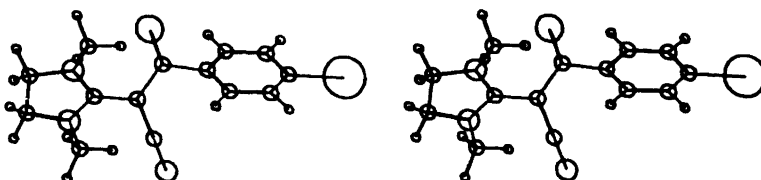


Fig. 4. Stereoscopic pair of ICE.

tion, new bond lengths were calculated by (4), where $R_{\mu\nu}^\circ$ is a standard bond length,

$$R_{\mu\nu} = R_{\mu\nu}^\circ - 0.18 p_{\mu\nu} \quad (4)$$

1.517 Å for a C–C bond, 1.458 Å for a C–N bond, 1.365 Å for a C–O bond, and 1.773 Å for a C–S bond. The C–Br and C≡N bonds were not iterated. The calculations were repeated until self-consistent bond lengths were obtained, which only required a few cycles. The results are given in Table 10 together with the starting bond lengths and the experimental bond lengths. The agreement between the calculated and the experimental C=C bond length in TCE is quite satisfactory, and the same can also be said about the C–S bonds, for which even the difference in bond length is correctly

reproduced. The too large calculated C(8)–C(12) bond length can be ascribed to the use of $R_{\mu\nu}^\circ = 1.517$ Å for this bond, though C(12) is *sp*-hybridized. The too low calculated value for the C(4)–C(7) bond can at least partly be explained by the observed twisting of the benzene ring out of the plane through C(8), C(7), and O(1) of 32.1°. The twisting of the S(1)–C(9)–S(2) group (15.2°) is probably too small to affect the bond lengths significantly. With the adopted conformation the S(1)–O(1) contact distance is 2.673 Å (van der Waals distance 3.25 Å) and C(11)–N(1) is 3.44 Å. H(111) is 2.54 Å from C(12) and 2.55 Å from N(1). Very short non-bonded interactions between sulfur and oxygen have been found earlier, *e.g.* 2.64 Å in two 2-acyl-methylene-1,3-dithietans,^{25–26}

Table 9. Parameters (eV).

Atom	$W_{\mu\mu}^\circ$	$\gamma_{\mu\mu}$	Bond ($\mu-\nu$)	$\beta_{\mu\nu}^\circ$	$\gamma_{\mu\nu}^\circ$	$\delta_{\mu\nu}^W$	$\delta_{\mu\nu}^\beta$	$\delta_\mu(\gamma)$	$\Delta W_\mu(\gamma)$	$\Delta W_\gamma(\mu)$	R_0 (Å)	Ref.
C	-9.89	11.97	C–C	-2.42	6.91	9.22	3.05	-3.99	0.07	0.07	1.397	33
N	-12.57	15.44	C–N	-2.72	7.16	5.6	2.6	-3.99	0.03	0.14	1.338	34
N	-8.52	15.44	C–N	-2.25	6.34	5.6	2.6	-3.99	0.03	0.14	1.338	34
O	-19.60	18.89	C–O	-2.46	9.33	0	0	0	-0.71	0	1.22	35
S	-10.62	9.58	C–S	-1.37	7.28	9.22	3.05	-3.99	-0.70	0	1.714	36
Br	-11.25	9.35	C–Br	-1.84	6.42	0	0	0	-2.01	0	1.880	37

2.41 Å in a 3-acetylmethylene-1,2-dithiole²⁷ and 2.78 Å in *o*-carboxyphenyl methyl sulfoxide.²⁸ The nature of this attractive force has been discussed by Kapecki and Baldwin²⁹ in terms of EHT calculations, and by Pfister-Guillouzo *et al.*³⁰ in terms of CNDO/2 calculations. The EHT calculations give no conclusive result, and the latter authors conclude that introduction of *d* orbitals in the basis set is necessary to get a proper description of the O...S interaction.

In the benzene ring H(31) is 2.56 Å from C(12) but 2.91 Å from N(1). Whereas thus C(12) has the same hydrogen packing contacts from two sides, the surrounding of N(1) is less symmetrical. This might explain the observed deviation of the C(8)–C(12)–N(1) angle from 180°. H(51) is 2.52 Å (van der Waals distance 2.72 Å) from O(1).

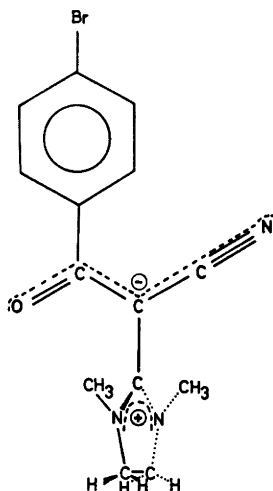


Fig. 5. ICE in the 90° twisted state.

For ICE, the C=C bond length calculated for a planar molecule is 1.388 Å. The difference between this and the experimental value of 1.448 Å must largely be ascribed to a steric interference between the N-methyl groups on one side and the carbonyl and cyano groups on the other causing a considerable twist (41.1°) of the molecule around the double bond. The C(10)–O(1) distance is 2.90 Å compared with the van der Waals distance 3.22 Å, and the C(11)–N(1) distance is 3.46 Å. The shortest O(1)···H distance is 2.27 Å and the shortest N(1)···H distance 2.67 Å. Evidently the interaction with the carbonyl group is the most important one. A case of a twisted double bond, which is only slightly stretched (to 1.345 Å), has recently been reported³¹ but this bond is a member of a polycyclic ring system, which may well restrict its expansion.

The experimental C(9)–N(2) and C(9)–N(3) bonds are considerably shorter than those calculated for the planar molecule. This can be ascribed to the twist and reflects the greater contribution in the actual molecule of the amidinium ion structure, which is postulated to stabilize the 90° twisted molecule¹⁴ (Fig. 5). This is compatible with the almost planar arrangement of O(1), C(7), C(8), C(12), and N(1). The imidazolide group is also nearly planar whereas it for instance in 1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine³² is considerably puckered. A larger polarization in ICE than in TCE is shown both by experimental and calculated bond lengths in the electron attracting part of the molecule (Table 10). Similarly, ICE shows a more extensive charge separation in the calculated π -electron distribution (see Fig. 6 for the distribution of

Table 10. Bond lengths (Å).

Molecule I			Experimental	Molecule II			Experimental
Bond	PPP Initial	Final		Bond	PPP Initial	Final	
C ₈ –C ₉	1.340	1.362	1.369	C ₈ –C ₉	1.340	1.388	1.448
C ₉ –S ₁	1.730	1.729	1.724	C ₉ –N ₂	1.400	1.378	1.324
C ₉ –S ₂	1.730	1.736	1.752	C ₉ –N ₃	1.400	1.386	1.332
C ₁₂ –C ₈	1.450	1.467	1.427	C ₁₂ –C ₈	1.450	1.456	1.410
C ₇ –C ₈	1.450	1.465	1.490	C ₇ –C ₈	1.450	1.440	1.423
C ₇ –O ₁	1.220	1.232	1.212	C ₇ –O ₁	1.220	1.242	1.235
C ₄ –C ₇	1.460	1.469	1.502	C ₄ –C ₇	1.460	1.471	1.514

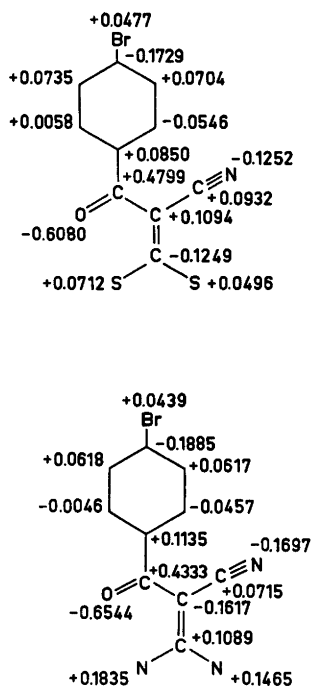


Fig. 6. Formal π -electron charges in TCE (above) and ICE (below).

formal charges). In TCE, the sulfur atoms donate 0.05 and 0.07 electronic units, respectively, whereas in ICE the figures for the nitrogen atoms are 0.15 and 0.18 units. In the latter compound, C(9) is also positive, indicating a partial formation of the amidinium ion structure already in the ground state, whereas in TCE this atom is negative.

Table 11. Intermolecular Br \cdots H, O \cdots H, N \cdots H and H \cdots H contacts less than 3 Å (TCE). i refers to the equivalent position $-x, \frac{1}{2}+y, -z$.

A	B	Unit translation of atom B	Å
Br(1)	H(113 ⁱ)	(2, -1, 1)	2.97
O(1)	H(21)	(-1, 0, 0)	2.64
O(1)	H(102)	(0, 0, -1)	2.94
N(1)	H(113)	(0, 0, -1)	2.98
H(31)	H(103)	(1, 0, 0)	2.92
H(51)	H(102)	(0, 0, -1)	2.95
H(51)	H(113 ⁱ)	(1, -1, 1)	2.94
H(101)	H(111)	(-1, 0, 0)	2.85
H(103)	H(111)	(-1, 0, 0)	2.72
H(103)	H(112)	(-1, 0, 0)	2.41

Table 12. Intermolecular Br \cdots H, O \cdots H, N \cdots H, C \cdots H and H \cdots H contacts less than 3 Å (ICE). i, ii, and iii refer to the equivalent positions $-x, -y, -z, -x, \frac{1}{2}+y, \frac{1}{2}-z$ and $x, \frac{1}{2}-y, \frac{1}{2}+z$.

A	B	Unit translation of atom B	Å
Br(1)	H(101 ⁱⁱⁱ)	(-1, 0, -1)	3.00
Br(1)	H(132 ⁱ)	(1, 1, 0)	2.88
O(1)	H(21 ⁱⁱⁱ)	(0, 0, 0)	2.36
O(1)	H(111 ⁱⁱ)	(1, -1, 0)	2.85
O(1)	H(141 ⁱⁱ)	(1, -1, 0)	2.63
O(1)	H(142 ⁱⁱⁱ)	(0, 0, -1)	2.36
N(1)	H(31 ⁱ)	(1, 1, 0)	2.65
N(1)	H(51 ⁱ)	(0, 1, 0)	2.89
N(1)	H(61 ⁱ)	(0, 1, 0)	2.63
N(1)	H(103 ⁱ)	(1, 1, 0)	2.82
N(1)	H(131 ⁱⁱ)	(1, 0, 0)	2.42
C(1)	H(102 ⁱ)	(1, 1, 0)	2.96
C(3)	H(112 ⁱⁱⁱ)	(0, 0, -1)	2.82
C(4)	H(112 ⁱⁱⁱ)	(0, 0, -1)	2.94
C(6)	H(101 ⁱⁱⁱ)	(-1, 0, -1)	2.91
C(6)	H(102 ⁱ)	(1, 1, 0)	2.89
C(7)	H(21 ⁱⁱⁱ)	(0, 0, 0)	2.80
C(12)	H(31 ⁱ)	(1, 1, 0)	2.78
H(21)	H(141 ⁱ)	(1, 1, 0)	2.46
H(31)	H(131 ⁱⁱⁱ)	(0, 0, -1)	2.57
H(31)	H(142 ⁱⁱⁱ)	(0, 0, -1)	2.59
H(61)	H(101 ⁱⁱⁱ)	(-1, 0, -1)	2.32
H(61)	H(111 ⁱ)	(0, 1, 0)	2.83
H(61)	H(113 ⁱ)	(0, 1, 0)	2.43
H(111)	H(101 ⁱⁱ)	(1, 0, 0)	2.80
H(141)	H(111 ⁱ)	(1, 1, 1)	2.94
H(141)	H(112 ⁱ)	(1, 1, 1)	2.81
H(141)	H(142 ⁱ)	(1, 1, 1)	3.00
H(142)	H(111 ⁱ)	(1, 1, 1)	2.54

From Table 11 it is evident that the most important intermolecular contacts of TCE involve the methyl hydrogens. There are thus no hydrogen packing distances less than 3 Å between benzene rings.

Table 12 gives the shortest intermolecular distances in ICE. Here the hydrogen atoms of one benzene ring are in packing contact with those of other benzene rings as well as with those of CH₂- and CH₃-groups. O(1) has apart from the intramolecular interaction with H(103) of 2.27 Å also other very short distances to H(21) (2.36 Å) and H(142) (2.36 Å).

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