The Crystal and Molecular Structure of *N,N*-Diethyl-*p*-nitrosoaniline

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The crystal and molecular structure of *N,N*-diethyl-*p*-nitrosoaniline has been determined from X-ray diffraction data collected at -165°C and refined by least-squares methods. The space group is $P2_1/n$ with cell dimensions $a=14.339(5)$ Å, $b=9.921(2)$ Å, $c=13.670(4)$ Å and $\beta=87.16(2)^{\circ}$ at -165°C . The final R factor was 5.6 %. The asymmetric unit contains two molecules which are slightly different as to the conformation in the diethylamino groups. Slight disordering in the nitroso groups gives an "average" molecular structure having near C_2 symmetry. Apparently the disorder does not prevent elucidation of physically meaningful bond lengths and angles in the diethylaminophenyl part of the molecule. This seems also to be the case for the nitroso group in one of the molecules when refining with "high" angle data. The molecular structure is consistent with a strong charge displacement from the diethylamino group to the nitroso group.

The present structure investigation of *N,N*-diethyl-*p*-nitrosoaniline (I) is part of a series of investigations of *C*-nitroso compounds. Previously the oxime tautomer of *p*-nitrosophenol and three of its salts (Ref. 1 and references therein), 5-nitrososalicylic acid,² *N,N*-dimethyl-*p*-nitrosoaniline (II)³ and its hydrochloride (III),⁴ and the compound *N,N,N',N'*-tetramethyl-1,5-diamino-4-nitrosobenzene (IV)⁵ have been investigated.

In the hydrochloride (III) the nitroso oxygen atom is protonated and the molecule has a pronounced *para* quinonoid structure (oxime form).⁴ This indicates a strong basic character of the nitroso group in the *p*-nitrosoanilines and keeps with the fact that these compounds often react as *para* quinonoid zwitterions.⁶ Noteworthy is the hydrolysis giving an amine and

a salt of *p*-nitrosophenol. The fact that additional base is not required for the condensation with reactive methylene groups [(II) is a reagent for these] giving anils is another outstanding evidence for the basic character (Ref. 6, p. 278). For (IV) a similar *intra*-molecular condensation yielding a benzimidazole severely obstructs isolation. The investigation of this compound showed the N–O bond to be much longer than a "pure" NO double bond [$1.276(2)$ Å]. The X-ray study of the methyl analog to the title compound, *i.e.* (II), showed the crystal to be disordered. Owing to this the structural results do only give indications as to the degree of *intra*-molecular charge displacement.³

EXPERIMENTAL

Suitable prismatic crystals were obtained by sublimation using a "cold finger". A preliminary film investigation at room temperature showed monoclinic symmetry, space group $P2_1/n$ and unit cell dimensions deviating a few per cents from those determined at liquid nitrogen temperature.

All the data were collected and the unit cell constants determined using a well developed crystal of dimensions $0.50 \times 0.10 \times 0.10$ mm³. Apart from the following details the experimental conditions were as those described in Ref. 5.

The temperature at the crystal site was -165°C . The scan limits were $2\theta(\alpha_1) - 1.0^{\circ}$ and $2\theta(\alpha_2) + 1.0^{\circ}$ and a quadrant of reciprocal space was examined. Reflections up to 60° in 2θ were measured and only those having integrated counts larger than a preset value during a 2 s scan over the peak. Out of 2588 unique reflections measured 1835 had intensities larger than $2.5\sigma(I)$ where $\sigma(I)$ is the estimated standard deviation of the intensity based on counting statistics adding 2 % uncertainty due to

experimental fluctuations. The atomic scattering factors for the heavy atoms were those of Doyle and Turner⁷ and for hydrogen those of Stewart *et al.*⁸ All programs except for the ORTEP program (Ref. 11 in Ref. 5) and the MULTAN program⁹ applied during the investigation are described in Ref. 10.

CRYSTAL DATA

N,N-Diethyl-*p*-nitrosoaniline, $C_{10}H_{14}N_2O$, monoclinic, space group $P2_1/n$ (No. 14). Dimensions of the unit cell at -165°C : $a = 14.339(5)$ Å, $b = 9.921(2)$ Å, $c = 13.670(4)$ Å and $\beta = 87.16(2)^\circ$; $V = 1944.3$ Å³, $M = 178.24$, $F(000) = 768$, $D_{\text{calc}} (-165^\circ\text{C}) = 1.218$ g cm⁻³, $Z = 8$.

STRUCTURE DETERMINATION

The structure was determined by direct methods.^{9,10} Using an ordered model anisotropic full matrix least-squares refinement with the heavy atoms yielded a conventional R factor of 11 %. At this stage hydrogen atoms were included. Their parameters refined smoothly starting from values estimated from stereochemical considerations. The refinement with all the observed reflections and all the atoms converged after a few cycles (alternately refining different groups) yielding $R = 0.075$ a weighted R_w factor of 0.064 and a goodness of fit S of 2.2. The estimated standard deviations (e.s.d.'s) in the bond lengths were in the range 0.005–0.009 Å and all bond lengths and angles but those involving the nitroso group atoms seemed reasonable. The C–NO and the N–O bond lengths, however, were respectively astonishingly long and unreasonably short in both molecules in the asymmetric unit (molecule A and molecule B). In molecule A the separations were 1.475(7) and 1.212(6) Å and in molecule B 1.585(9) and 1.153(7) Å for, respectively, the C–NO and the N–O bond length. In a subsequent Fourier synthesis the C–NO bond lengths became "normal": 1.385 Å for molecule A and 1.405 Å for molecule B.

A difference Fourier map was then calculated using "high angle" parameters and a low angle data set (above and below 0.40 in $\sin \theta/\lambda$). The map showed two residual peaks of about 1 eÅ⁻³ whose positions were related to those of the oxygen atoms by a 2-fold rotation about a line through the atoms C1, C4 and N1. Inte-

gration over several peaks in Fourier maps indicated that the oxygen atom is situated with an occupational factor of 0.27 for molecule B and 0.19 for molecule A in this other position, O4*. These figures were obtained assuming gross atomic charges of 8.25 e at O4 and 6.95 e at N4 in both molecules.

By analogy with other monomeric nitrosobenzenes investigated it was assumed that (I) has unequal exocyclic angles at C4 (usually differing 7–10°). It was therefore decided to modify the model by including both an O4* and a N4* pseudo atom. Their initial positional parameters were estimated from stereochemical considerations. In the first refinement cycles with the disordered model the multiplicities cited were used, and all atoms were included (alternately). The nitroso group atoms were treated isotropically. This was also the case in a subsequent refinement varying (without constraint) only the parameters for O4, N4 and the pseudo atoms. Different occupational factors were tried in a regular manner and the best R factors were obtained with 0.160 for the pseudo atoms in molecule A (0.840 for O4A and N4A) and 0.278 for the pseudo atoms in molecule B (0.722 for O4B and N4B). Using these occupational factors also the most reasonable temperature factors and structural results were obtained (reasonable in the sense that the results for A or B resembled closely those for A* or B*). In the remaining refinement these occupational factors and the parameters arrived at for the pseudo atoms were retained. The latter was considered appropriate as a separate refinement with isotropic pseudo atoms and anisotropic heavy atoms of molecule B yielded unreasonable temperature factors for the nitroso group atoms. Treating the O4 and the N4 atoms anisotropically the final refinement (alternately refining different groups) converged yielding a R , R_w and S factor being significantly¹¹ smaller than that obtained for the ordered model: $R = 0.56$, $R_w = 0.047$ and $S = 1.69$. Final parameters are given in Table 1 and 2.

Magnitudes and directions of the principal axes of the vibrational ellipsoids are indicated in Fig. 1. A rigid body analysis of the entire molecule shows a fairly good agreement between observed and calculated vibrational tensor elements: $\Delta U_{\text{rms}} = 0.0038$ Å² for molecule

Table 1. Fractional atomic coordinates and thermal parameters for the non-hydrogen atoms. The temperature factors are expressed as: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{33})]$. Estimated standard deviations in parentheses.

ATOM	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O4A	.38366(21)	.81511(32)	-.06229(24)	.0400(28)	.0396(22)	.0369(21)	-.0024(17)	-.0114(17)	.0029(18)
N1A	.57749(18)	.79159(31)	.20643(20)	.0220(17)	.0239(17)	.0206(17)	-.0012(16)	-.0050(14)	-.0010(15)
N4A	.28286(28)	.79861(42)	.02780(31)	.0502(27)	.0368(27)	.0365(26)	.0013(23)	-.0043(22)	.0042(24)
C1A	.50834(24)	.79488(36)	.21619(25)	.0261(21)	.0142(20)	.0226(21)	-.0015(18)	-.0037(17)	-.0040(18)
C2A	.52852(24)	.81353(37)	.11429(25)	.0293(22)	.0204(25)	.0177(20)	.0027(18)	-.0005(17)	.0024(18)
C3A	.45741(26)	.81653(38)	.05030(25)	.0309(24)	.0193(23)	.0200(21)	.0044(18)	-.0003(19)	.0016(17)
C4A	.36806(25)	.80046(38)	.00307(27)	.0272(22)	.0200(23)	.0314(24)	.0069(19)	-.0115(19)	-.0016(19)
C5A	.34368(24)	.78147(39)	.18263(28)	.0226(20)	.0207(23)	.0350(24)	-.0001(20)	-.0023(18)	.0013(22)
C6A	.41303(23)	.77850(37)	.24847(29)	.0255(21)	.0212(20)	.0202(21)	.0002(19)	-.0002(17)	.0005(19)
C7A	.07646(24)	.79716(39)	.24615(25)	.0229(20)	.0327(23)	.0262(22)	.0033(20)	.0053(17)	.0015(20)
C8A	.05863(25)	.78171(40)	.38615(25)	.0375(23)	.0293(22)	.0126(19)	-.0012(21)	.0023(16)	-.0018(19)
C9A	.71186(26)	.84055(40)	.23129(30)	.0332(24)	.0344(25)	.0436(27)	-.0091(21)	-.0030(20)	.0005(22)
C10A	.8531(17)	.83619(38)	.42144(27)	.0538(28)	.0236(22)	.0225(21)	.0013(21)	-.0039(20)	.0006(19)
O4B	.10606(25)	.28733(45)	-.00534(28)	.0361(24)	.0527(28)	.0506(27)	-.0081(23)	-.0053(20)	.0059(25)
N1B	.42604(19)	.27985(38)	.19213(20)	.0276(18)	.0146(16)	.0227(17)	.0021(16)	-.0064(15)	-.0025(15)
N4B	.14098(31)	.31384(49)	-.07186(32)	.0293(27)	.0380(33)	.0356(29)	-.0011(24)	.0026(24)	.0007(25)
C1B	.38712(24)	.20220(37)	.12994(25)	.0246(20)	.0237(21)	.0179(19)	.0025(20)	.0019(17)	.0001(19)
C2B	.32708(24)	.40527(37)	.00709(26)	.0243(22)	.0261(24)	.0271(22)	.0039(18)	-.0044(19)	.0014(19)
C3B	.28671(26)	.40747(40)	.02613(28)	.0257(24)	.0364(28)	.0299(25)	.0050(20)	.0001(20)	.0053(21)
C4B	.21104(25)	.28076(59)	.00194(26)	.0179(20)	.0501(29)	.0196(22)	.0044(24)	-.0040(17)	.0041(23)
C5B	.23940(26)	.16687(41)	.03084(28)	.0224(22)	.0428(28)	.0260(23)	-.0007(19)	.0004(19)	.0157(21)
C6B	.30995(25)	.18069(37)	.18386(28)	.0262(22)	.0250(22)	.0260(23)	-.0020(18)	.0018(19)	-.0042(19)
C7B	.47282(27)	.40399(37)	.22334(27)	.0392(25)	.0239(24)	.0277(23)	.0045(20)	-.0108(20)	.0002(19)
C8B	.46206(25)	.15356(36)	.25373(27)	.0314(23)	.0211(22)	.0262(22)	.0060(19)	-.0007(19)	.0015(19)
C9B	.55197(26)	.44626(39)	.15297(30)	.0317(24)	.0273(24)	.0492(27)	-.0033(19)	-.0158(21)	-.0030(22)
C10B	.40899(27)	.11503(39)	.32813(27)	.0406(26)	.0295(23)	.0256(23)	.0118(21)	-.0056(20)	.0024(19)

Table 2. Fractional atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the hydrogen atoms and the nitroso group atoms in their less preferred sites. Estimated standard deviations in parentheses.

Atom	x	y	z	B
H2A	0.5914(21)	0.8286(29)	0.0045(22)	1.6(7)
H3A	0.4780(21)	0.8300(31)	-0.0159(25)	2.1(8)
H5A	0.2751(21)	0.7688(31)	0.2080(21)	2.1(7)
H6A	0.3944(19)	0.7642(30)	0.3187(21)	1.4(7)
H71A	0.7090(21)	0.7521(29)	0.2975(22)	1.6(7)
H72A	0.6894(21)	0.7406(32)	0.1814(24)	2.5(8)
H81A	0.6092(23)	0.8287(33)	0.4203(24)	3.0(9)
H82A	0.4971(22)	0.8367(32)	0.4102(23)	2.5(8)
H91A	0.7789(25)	0.9388(34)	0.2069(25)	3.3(9)
H92A	0.7027(25)	1.0001(38)	0.2935(29)	4.1(1.0)
H93A	0.6767(25)	0.9885(36)	0.1814(27)	3.8(1.0)
H101A	0.5389(22)	0.6348(36)	0.4910(28)	3.3(9)
H102A	0.6094(23)	0.5820(34)	0.3967(24)	2.6(9)
H103A	0.4986(25)	0.5932(35)	0.3945(26)	3.5(1.0)
H2B	0.3278(21)	0.0787(34)	0.1296(23)	1.9(8)
H3B	0.2105(20)	0.0851(30)	0.0220(21)	1.2(7)
H5B	0.2356(23)	0.4911(33)	-0.0084(25)	2.6(8)
H6B	0.3523(22)	0.4908(33)	0.1050(23)	2.1(8)
H71B	0.5318(22)	0.1733(29)	0.2512(22)	1.9(7)
H72B	0.4612(20)	0.4612(31)	0.1038(22)	1.5(7)
H81B	0.4959(23)	0.3875(35)	0.2811(26)	2.7(9)
H82B	0.4225(19)	0.4772(31)	0.2372(20)	1.1(7)
H91B	0.4054(22)	0.1902(34)	0.3742(24)	2.4(8)
H92B	0.4420(25)	0.0480(40)	0.3656(27)	4.0(1.0)
H93B	0.3440(29)	0.0816(40)	0.3231(29)	5.2(1.2)
H101B	0.5978(23)	0.3767(37)	0.1354(25)	3.0(9)
H102B	0.5838(25)	0.5267(39)	0.1799(27)	4.2(1.0)
H103B	0.5309(24)	0.4725(36)	0.0863(27)	3.3(9)
O4A*	0.2277(13)	0.8027(18)	0.0219(13)	3.9(4)
N4A*	0.3130(14)	0.8099(22)	-0.0026(18)	2.1(4)
O4B*	0.1086(07)	0.3704(11)	-0.0964(07)	3.4(2)
N4B*	0.1381(11)	0.2606(16)	-0.0620(11)	3.0(3)

A and $\Delta U_{\text{rms}} = 0.0044 \text{ \AA}^2$ for molecule B. Exclusion of the terminal methyl carbon atoms did not improve the agreement while this was the case when excluding the O4 and N4 atoms ($\Delta U_{\text{rms}} = 0.0025 \text{ \AA}^2$ for both molecules). For the entire molecule the r.m.s. "eigenvalues" of T are 0.17, 0.15 and $0.13 \text{ \AA}^2$ as to molecule A and 0.17, 0.16 and $0.14 \text{ \AA}^2$ for molecule B while the r.m.s. "eigenvalues" of L are 2.9, 2.2 and 1.8° for molecule A and 3.2, 2.1 and 1.3° for molecule B.

Disregard of low angle scattering has a marked shortening effect on the C4–N4 bond

Fig. 1. 50 % probability ellipsoids and numbering of atoms. The pseudo atoms are dotted.

Table 3. The dependency upon the inner cutoff value of $\sin \theta/\lambda$ for the bond lengths (Å) and angles (°) involving the O4 and the N4 atom. The estimated standard deviations are in parentheses.

Data set	O4—N4	N4—C4	O4—N4—C4	N4—C4—C5
Molecule A				
1	1.253(5)	1.437(5)	110.9(4)	111.8(4)
2	1.254(5)	1.432(5)	111.2(4)	112.1(3)
3	1.255(6)	1.406(7)	112.4(4)	112.6(4)
4	1.269(11)	1.382(11)	112.6(6)	112.7(6)
Molecule B				
1	1.216(5)	1.458(6)	109.9(4)	112.0(4)
2	1.217(6)	1.451(6)	110.3(4)	112.2(4)
3	1.221(8)	1.432(7)	111.0(5)	112.0(5)
4	1.225(13)	1.417(9)	111.7(8)	111.0(7)

Data set	$\sin \theta/\lambda$ range	Number of reflections	Scale factor	$R \times 100$	$R_w \times 100$	S
1	0.0—0.7	1835	0.656	5.6	4.7	1.7
2	0.2—0.7	1712	0.642	5.8	4.8	1.5
3	0.3—0.7	1446	0.659	6.1	5.2	1.4
4	0.4—0.7	1029	0.684	6.3	5.3	1.3

length and a widening effect on the C4—N4—O4 angle. This can be seen from Table 3 where values from several refinements using different inner cutoff values for $\sin \theta/\lambda$ are listed. The contribution from the valence-electrons to the total integrated scattering of nitrogen decreases from about 30 to less than 10 % when excluding data below 0.4 in $\sin \theta/\lambda$ ($B_{iso} = 2.5 \text{ Å}^2$). Then, the error in the positional parameters resulting from the extended "overlap" of the valence-electron clouds of N4 and N4* is

probably less using only data above 0.4 in $\sin \theta/\lambda$ than when using all the data.

Bond lengths and angles involving the non-hydrogen atoms are given in Table 4. The e.s.d.'s were obtained from the correlation matrix of the final refinement cycle with these atoms. The C—H bond lengths obtained are in the range 0.89—1.07 Å with e.s.d.'s of 0.03 Å. Deviations of atoms from least-squares planes are given in Table 5.

Fig. 2. A stereoscopic illustration of the structure. The shortest O...H contacts are indicated by fine lines.

Table 4. Bond lengths (Å) and angles (°).

A		B	A		B
In the diethylaminophenyl part					
N1—C1	1.358(4)	1.345(4)	C1—C2	1.420(5)	1.425(5)
N1—C7	1.473(4)	1.480(4)	C2—C3	1.376(5)	1.372(5)
N1—C8	1.460(4)	1.469(4)	C3—C4	1.386(5)	1.393(5)
C7—C9	1.519(5)	1.520(5)	C4—C5	1.393(5)	1.397(5)
C8—C10	1.523(5)	1.512(5)	C5—C6	1.375(5)	1.360(5)
			C6—C1	1.425(5)	1.426(5)
C1—N1—C7	121.1(3)	122.9(3)	C1—C2—C3	120.3(3)	120.8(4)
C1—N1—C8	122.7(3)	121.8(3)	C2—C3—C4	121.2(3)	120.8(4)
C7—N1—C8	116.3(3)	115.4(3)	C3—C4—C5	119.5(3)	119.2(3)
N1—C7—C9	112.7(3)	111.5(3)	C4—C5—C6	120.7(3)	121.1(4)
N1—C8—C10	112.4(3)	112.3(3)	C5—C6—C1	120.6(3)	121.0(4)
N1—C1—C2	121.2(3)	121.8(4)	C6—C1—C2	117.7(3)	117.1(3)
N1—C1—C6	121.1(3)	121.1(4)			
In the nitroso group of molecule A by use of Data set 4					
O4—N4	1.27(1)		O4—N4—C4	112.6(6)	
N4—C4	1.38(1)		N4—C4—C3	129.1(6)	
			N4—C4—C5	112.7(6)	
In the nitroso group with atoms in the less preferred position					
O4*—N4*	1.25(2)	1.27(2)	O4*—N4*—C4	109(1)	109(1)
N4*—C4	1.42(1)	1.41(1)			
In the nitroso group when refining with all atoms in molecule B including the pseudo atoms O4* and N4*					
O4—N4	1.220(14)		O4*—N4*	1.27(4)	
N4—C4	1.435(19)		N4*—C4	1.43(4)	

Table 5. Deviations (Å) of atoms from a least-squares plane defined by the benzene ring atoms.

Atom	A	B
O4	−0.024	0.102
N1	−0.003	0.009
N4	−0.016	0.028
C1	0.002	0.002
C2	−0.003	−0.011
C3	0.002	0.008
C4	0.000	0.004
C5	−0.001	−0.013
C6	0.002	0.009
C7	−0.114	0.081
C8	0.092	−0.054
C9	1.230	−1.304
C10	−1.273	1.312
O4*	0.08	−0.08
N4*	0.01	−0.01

DISCUSSION

Fig. 2 shows the packing of molecules in the crystal. All intermolecular contacts, including those involving the pseudo atoms, are of van der Waals type. Each of the two independent molecules form chains by lying head to tail along the *n*-glides. An approximately linear NC—H...O contact (3.450 and 3.390 Å for, respectively, the A and B molecule with oxygen in its preferred site) constitutes the link between the molecules in the chains and it seems as if this contact has an orienting effect on the packing along the chains.

The type of disorder in the present structure parallels that found in the crystals of *N,N*-dimethyl-*p*-nitrosoaniline (II) in that the nitroso group atoms occupy two positions related by twofold rotational symmetry about the line through N1, C1 and C4. This similarity is proba-

bly a consequence of the similar packing pattern for (I) and (II) with only van der Waals contacts⁸ to the nitroso group in both its orientations. However, whereas there is no preference for one of the orientations in (II) this is the case for both the molecules of (I). It seems as if the NO group experiences a discriminating difference between its possible types of environment in the latter case. Sterically the difference between the two immediate surroundings consists in fewer contacts to hydrogen atoms and a less regular coordination of these in the less preferred site. However, because of the long range effect of the coulombic and dispersion forces there are four types of environment which should be considered: both, only one (two types) and none of the NO groups having the preferred orientation. These four possibilities correspond to the four ordered structures AB, A*B, AB* and A*B* composing the disordered structure. The portion (*p*) of the individual structure type in the crystal is within the range 0.72–0.56 for AB, 0.28–0.12 for AB* and 0.16–0.0 for A*B and A*B* (or 0.60, 0.24, 0.12 and 0.04, respectively, if $p_{AB}/p_{AB^*} = p_{A^*B}/p_{A^*B^*}$). If this is a distribution resulting from dynamic disorder at the temperature of formation of the crystal (85 °C) the energy difference between for example AB and AB* is at least about 0.5 kcal/mol. Any difference between calculated packing energies is less than 0.10 kcal/mol using the Kitaigorodsky universal potential¹³ for the dispersion energy and the expression $(kq_iq_j/r_{ij})\exp(r_{ij}^0 - r_{ij})$ (Ref. 13) for the Coulomb energy. As it is rather unlikely the disorder being dynamic at temperatures appreciably below the melting point this indicates that the observed distribution is mainly a result of other factors. The calculated dispersion energies amounts to –14.4 to –14.5 kcal/mol and the Coulomb energies to 1.0–1.2 kcal/mol. In the expression for the Coulomb energy *k* is a constant (332.1 kcal/mol erg), *q* is the net atomic charge from INDO calculations based upon the found molecular geometry (gross atomic populations in Table 6) and *r*⁰ is the equilibrium *inter*-molecular distance.¹³

The molecular structure. Both the benzene rings and both the C1N1(C7)C8 fragments are planar within the accuracy of the experiment. The amino nitrogen atoms do not deviate

Table 6. Gross atomic populations from INDO calculations based upon the geometry of molecule A.

O4	8.21	C6	6.08
N1	7.17	C7	5.83
N4	6.95	C8	5.82
C1	5.82	C9	5.99
C2	6.07	C10	6.00
C3	5.94	H(C _{ar})	1.01
C4	5.97	H(C7, C8)	1.04
C5	5.96	H(C9, C10)	1.00

significantly from the ring plane and the twist about the Et₂N–C bonds is only a few degrees. The nitroso group atoms of molecule A and the N4B atom seem to be in the ring plane while the deviation of the O4B atom is probably large enough as to be considered significant. The methyl carbon atoms deviate nearly maximally (within the frames set by normal ethyl group geometry) to either side of the C1N1(C7)C8-plane in both molecules. This conformation is similar to that of the *N,N*-diethyl-anilino moiety of a pyrazoline dye (V)¹⁴ and is probably that which gives least crowding. Fig. 3 shows that the difference between the two independent molecules as to their conformation are only of the order of a few degrees. It is noteworthy however that it seems to be connected to the NC–H...O contacts mentioned above.

Apart from the C–NO and the N–O bond length there are not any formally significant differences between corresponding bond lengths in the two molecules. Neither are there any significant differences between chemically equivalent bond lengths within the two molecules. This is taken to indicate that these bond lengths are physically meaningful and influenced negligibly by the disorder.

A comparison of (I) and the *para* substituted *N,N*-dialkylanilines (V) and methyl orange¹⁵ shows that these three compounds have very similar bond lengths. Probably this similarity is due to a nearly equal electron-accepting ability of the *para* substituents (a 4-imino-2-pyrazolin-5-one group in (V) and an azophenyl group in methyl orange). This is confirmed by comparing (I) and the compound *p*-dimethyl-amino-phenyl-diphenylphosphine (VI)¹⁶ where a weakly electron-accepting PPh₂ group is in

Fig. 3. Dihedral angles in the diethylamino groups. The protons shown are those involved in the NC-H...O contacts mentioned in the text.

para position to the dialkylamino group. Most C-C bond lengths in (I) deviate about 0.02 Å from corresponding bond lengths in (VI) which seem to be of only one type (the mean value is 1.393 Å with an e.s.d. of 0.004 Å which is identical to the e.s.d. in the separate bond lengths). In (I), (V) and methyl orange the bond lengths are of three types (the mean value for both molecules of (I) is 1.396 Å with an e.s.d. of 0.022 Å for A and an e.s.d. of 0.027 Å for B); two being 0.02–0.03 Å longer, two being 0.02–0.03 Å shorter and two being very similar to the benzene separation. The two former and the two latter bonds are adjacent to respectively the R_2N-C bond and the $C-NX$ bond [$X=O$ for (I), $X=N$ for methyl orange and $X=C$ for (V)]. In consistency with this the R_2N-C bond length in (I), (V) [1.355(2) Å] and methyl orange [1.365(6) Å] is about 0.02–0.03 Å shorter than that in (VI) [1.380(3)

Å]. For all the dialkylanilines mentioned the amino-nitrogen atom is trigonally hybridized and the twist about the $N-C_{ar}$ bond of only a few degrees.

Considering the inductive effect of the NO group the major cause of shorter C-C4 bonds than C-C1 bonds it seems as if a *para* quinonoid element is contributing appreciably to the π -resonance in (I). The INDO calculations mentioned above yielded π -bond orders being consistent with a lesser contribution of this element than actually observed: N1-C1: 0.40, C1-C2(6): 0.59, C2(6)-C3(5): 0.70, C3(5)-C4: 0.62, C4-N4: 0.31 and N-O: 0.93. The gross atomic populations calculated (in Table 6) indicate about equal net charge on the oxygen atom and the amino nitrogen atom. However, it seems probable that the oxygen atom actually is appreciably more negative than the amino nitrogen atom as the calculated dipole moment is substantially smaller than that measured in inert solution (5.1 D compared with 7.23 D). Possibly this discrepancy between theory and experiment may be attributed to the inadequacy of the one-electron configuration description of the molecular ground state used in the calculations.

The differences between corresponding bond lengths in (I) and the hydrochloride of (II) resemble closely those between the *p*-nitroso-phenolate anions and *p*-benzoquinone monoxime.¹ They are, however, generally slightly larger than in the latter case.

The bond angles except for those involving the nitroso group atoms are very similar to those of (V). Owing to this similarity and the close resemblance of corresponding bond lengths in the diethylaminophenyl part of (I) and (V) it seems reasonable that also the C4-N bond lengths of the two compounds resemble each other. And this is the case if one considers the bond length in molecule A obtained by use of "high" angle data in the refinement [1.374(3) Å for (V) compared with 1.38(1) Å for (I)]. This bond length is also very similar to that in *N,N,N',N'*-tetramethyl-1,5-diamino-4-nitrosobenzene, (IV), [1.372(2) Å]; in consistency with the resemblance of the N-O bond lengths in (I) and (IV) [1.276(2) Å in (IV) compared with 1.27(1) Å for (I)].

It is worth mentioning that the N-O bond length from this investigation (1.27 Å) is very

Fig. 4. A plot of the N—O bond length R and the wave number $\tilde{\nu}$ of the ω normal mode involving essentially the NO group in the compounds NO^+ (A),¹⁷ NO (B),¹⁷ N_2O_3 (C),¹⁷ FNO (D),^{19, 17} ClNO (E),¹⁷ BrNO (F),¹⁷ HNO_2 (G),^{18, 17} CF_3NO (H),^{19, 6} CH_3NO (I),^{19, 6} HNO (J),^{20, 21} NCNO (K),^{20, 22} Me_2NNO (L),^{20, 23, 24} 5-nitrososalicylic acid (M),² (IV),^{5, 25} sodium *p*-nitrosophenolate trihydrate (N) (Ref. within Ref. 1), (III),^{4, 25} *p*-benzoquinone monoxime (O) (Ref. within Ref. 1 and Ref. 25), formaldoxime (P).^{20, 26} The least-squares line shown is for the ●-points (2.5 σ in R indicated with bars).

similar to an R_{NO} value obtained using IR spectroscopy and correlation of N—O bond lengths with the wave number of the normal ω mode involving essentially the NO group. The plot of R_{NO} against ω_{NO} in Fig. 4 shows a remarkable linearity between the two magnitudes if one excludes the points for NO^+ , NO and N_2O_3 (the confidence factor is 0.99). The least-squares line shown has the slope $-2.90 \times 10^4 \text{ Å}^2$ and the intercept 1.667 Å. Assuming inaccuracy only in R_{NO} with a mean e.s.d. of 0.003 Å the e.s.d. in the slope is $3 \times 10^3 \text{ Å}^2$ and in the intercept 0.004 Å. The KBr-IR spectrum of (I) is very similar to that of (II) and using the assignment of Knieriem²⁵ for (II) the wave number for ω_{NO} is set to 1380 cm^{-1} . Insertion of this value in the equation for the least-squares line gives the value 1.265 Å for R_{NO} in (I).

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