

On the Molecular Structure of N,N' -Di-*t*-butyl-1,2-ethanediimine, $(\text{CH}_3)_3\text{CN}=\text{CHCH}=\text{NC}(\text{CH}_3)_3$, as Studied by Gas Electron Diffraction

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According to a gaseous electron diffraction analysis, the majority of N,N' -di-*t*-butyl-1,2-ethanediimine molecules takes a *gauche* form, with respect to the central bond, which is characterized by a rotation of 65° from the *syn* form. The presence of a smaller amount of the *anti* form is also indicated. The arrangement around the double bonds is *trans*. The conformation around the C—N single bond is such that the C=N double bond and one of the C—C bonds of the adjacent *t*-butyl group are in the same plane. The following bond lengths and bond angles were determined with their standard deviations parenthesized: =C—C= 1.496(0.020) Å, C—H 1.117(0.005) Å, N=C 1.283(0.006) Å, N—C 1.468(0.016) Å, C—C 1.537(0.005) Å, =C—C=N 117.3(4.0)°, =C—C—H 116.4(1.5)°, C=N—C 122.8(1.5)°, N—C—C 109.4(0.6)°, and C—C—H 112.1(1.0)°.

Several recent studies show considerable interest toward the conformational properties of molecules with conjugated chains. In addition to the earlier established importance of the *anti* form (torsion angle $\tau=180^\circ$) in many systems,¹ there are results in increasing number indicating that it is the *gauche* conformer ($\tau\approx 60^\circ$) rather than the *syn* ($\tau=0^\circ$) that may be present as a second conformer in substantial amounts and even prevail in some cases (for examples and references see DISCUSSION). As the question about the origin of the conformational choice in these systems is not yet well settled, and steric interactions is one of

the important effects to be considered, it was found to be of interest to investigate the conformational properties of N,N' -di-*t*-butyl 1,2-ethanediimine, $(\text{CH}_3)_3\text{C}-\text{N}=\text{CH}-\text{CH}=\text{N}-\text{C}(\text{CH}_3)_3$, in the vapour phase.

EXPERIMENTAL

The sample of N,N' -di-*t*-butyl-1,2-ethanediimine was kindly supplied by Prof. H. tom Dieck (Institut für Anorganische Chemie, Universität Frankfurt). The electron diffraction patterns were taken with the Balzers apparatus KD-G2 in Oslo^{2,3} at the camera distances 50 and 25 cm. The nozzle temperature was about 80°C and the electron wavelength was 0.05852 Å. Four plates (Kodak electron image) from each camera distance were selected for analysis. The ranges of intensity data used were $1.25\leq s\leq 14.00\text{ \AA}^{-1}$ with $\Delta s=0.125\text{ \AA}^{-1}$ and $4.00\leq s\leq 28.5\text{ \AA}^{-1}$ with $\Delta s=0.25\text{ \AA}^{-1}$ corresponding to the two camera distances. The procedure of data reduction was as previously described.⁴ The modified experimental molecular intensities are shown in Fig. 1.

STRUCTURE ANALYSIS

The geometry of the models. All models had a twofold symmetry axis perpendicular to the central C—C bond (C_2 symmetry). The rotation angle τ around the central C—C bond was defined in such way that $\tau=0$ and $\tau=180^\circ$ correspond to *syn* and *anti* conformations of the N=C—C=N chain, respectively.

In most models the conformation around the C=N double bond was *trans*. The *cis*

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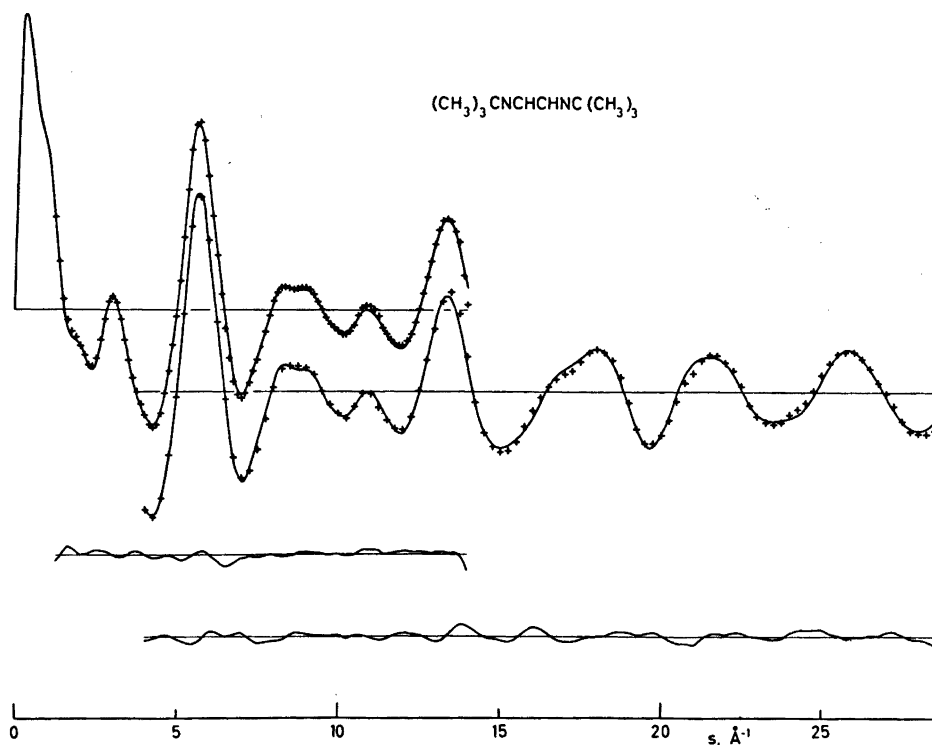


Fig. 1. Modified molecular intensities of *N,N'*-di-*t*-butyl-1,2-ethanediimine. Crosses: experimental (the upper and lower distributions correspond to the 50 and 25 cm camera ranges, resp.) Full lines: theoretical curves calculated from the parameters presented in Tables 1 and 2 for a mixture of 80 % *gauche* and 20 % *anti*. The difference curves are also shown.

Table 1. *N,N'*-Di-*t*-butyl-1,2-ethanediimine. Results of least squares refinement for the *gauche* ($\tau=65^\circ$) form (with 20 % *anti* form in the mixture). Bond lengths (r , Å), bond angles (\angle , °), and torsion angles (τ , ϕ , °). The standard deviations for the bond lengths refer to the last digit given.

N Type	Parameter	$\sigma_{\text{LS}}(r, \angle)^a$	$\sigma_{\text{LS}}^{\text{corr}}(r, \angle)^b$	l	$\sigma_{\text{LS}}(l)^a$	$\sigma_{\text{LS}}^{\text{corr}}(l)^b$
1 = C—C=	1.496	16	20	0.044		
2 C—H	1.117	3	5	0.073	3	5
3 N=C	1.283	3	6	0.029	5	8
4 N—C	1.468	10	16	0.042		
5 C—C	1.537	3	5	0.054	5	8
6 =C—C=N	117.3	3.1	4.0			
7 =C—C—H	116.4	1.3	1.5			
8 C=N—C	122.8	1.3	1.5			
9 N—C—C	109.4	0.6	0.6			
10 —C—C—H	112.1	0.6	1.0			
11 $\tau(\text{N}=\text{C}-\text{C}=\text{N})$	65.0	3.8	3.5			
12 $\phi(\text{C}=\text{N}-\text{C}-\text{C})$	0.0					

^a Standard deviations from the least squares refinement with diagonal weight matrix. ^b Standard deviations from the least squares refinement with off-diagonal elements also included in the weight matrix.¹⁷

conformation has also been tested but could be rejected with confidence.

Conformations around the C–N single bond were examined. As a result, the rotation form in which the C=N and C–C bonds of the C=N–C–C chain eclipse each other was accepted. The form in which the C=N bond is staggered by two of the C–C bonds of the *t*-butyl group could easily be ruled out by inspecting the experimental and theoretical radial distribution curves.

The following assumptions were made: All C–H bonds are of equal length and have the same mean amplitude of vibration (l value). The $-\text{C}(\text{CH}_3)_3-$ and the CH_3 -groups have local C_3 symmetry, and the pyramidal axes coincide with the extension of the N–C bond and the C–C bond, respectively. The C–H bonds of the methyl groups are staggered with respect to the C–C bonds of the *t*-butyl group to which they belong.

The bond lengths, bond angles and torsion angles characterizing the molecular geometry are listed in Table 1.

Experimental radial distribution. The experimental radial distribution curve is presented in Fig. 2. The first two peaks at about 1.2 and 1.5 Å obviously contain the contribution from the bond distances, the former corresponding to C–H and C=N, and the latter to C–N, C–C–, and C–C. Most of the rotation-independent distances between non-bonded atoms were expected to appear in the next peak at about 2.45 Å. The rotation-dependent distances could appear in this peak and up to very large values of r (8–9 Å) on the radial distribution curve. Unfortunately, no information could be read off directly from the experimental radial distribution curve. Its features were, however, instrumental in the analysis for testing models.

Trial structures. Various starting values for the bond lengths and bond angles have been used in the trial structures estimated on the basis of known structures and considering the experimental radial distribution. They were refined using fixed values for the torsion angle τ around the =C–C= bond. Later the constraint on τ was also removed.

REFINEMENTS AND RESULTS

The least squares method was applied to the modified molecular intensities.⁴ The modification function was $s/|f_c(s)|^2$. Unit weights were applied for the entire intensity interval.

All bond distances and bond angles together with the torsion angle τ could be refined simultaneously. However, when l values were also varied, some of them were kept constant, most often $r(=\text{C}=\text{C}=\text{C})$, $\angle=\text{C}=\text{C}=\text{H}$ and/or $\angle\text{C}=\text{C}=\text{H}$. The l values for the bonds =C–C= and C–N were assumed to be 0.044 and 0.042 Å, respectively, and not refined, while those for the other bonds were determined. The l values for the most important non-bond distances, N...C, C...C, and C...H, N...H with large occurrence ($n_{ij} \geq 6$), were allowed to vary in groups in separate refinements together with the geometrical parameters. The groups were formed from distances that occurred in the same peak or were closely spaced, and the l values in the group were coupled, *i.e.* the differences between them were kept constant at assumed values. Typical examples of groups of l values formed for simultaneous refinement are shown in Table 2. The l values for distances C...H and N...H with multiplicities less than six and H...H have not been refined, but in most cases more than one trial value has been tested. Values between 0.10 and 0.35 Å have been utilized in the final calculations.

The outer part of the radial distribution curve, say, $r > 5$ Å, was seen to be little sensitive to the rotation around the =C–C= bond. The distances involving either atoms C5 or C21 remain practically unchanged during rotation around the =C–C= bond since these atoms are very near the rotation axis. Also, the l values for these long distances are very uncertain. The interval between $r=2.8$ and 5 Å seemed to be the most important portion of the radial distribution curve in examining the rotation forms around the =C–C= bond. The rotation-dependent distances occurring in this region (*e.g.* N3...C20) made it possible to identify the *gauche* form with $\tau(\text{N}=\text{C}=\text{C}=\text{N})$ around 65° as preferred (Fig. 2).

The theoretical molecular intensity and radial distribution curves calculated for other conformers showed poorer agreement with the experimental data and refined often to un-

Table 2. *N,N'*-Di-*t*-butyl-1,2-ethanediiimine. Results of least squares refinement for the *gauche* ($\tau = 65^\circ$) form (with 20 % *anti* form in the mixture). Mean amplitudes of vibration for non-bonded distances in the $C_3CNCCNCC_3$ skeleton and distances C-H and N-H with a multiplicity of six or more. The standard deviations refer to the last digit given.

<i>N</i>	<i>i</i>	<i>j</i>	<i>n</i> _{ij}	<i>r</i> _{ij}	$\sigma_{LS}(r)^a$	$\sigma_{LS}^{corr}(r)^b$	<i>l</i> _{ij}	$\sigma_{LS}(l)^a$	$\sigma_{LS}^{corr}(l)^b$	Group
21	C4	H8	18	2.213	8	13	0.108	12	17	
22	C1	N19	2	2.362	15	19	0.077	8	9	i
23	C1	C4	2	2.410	16	20	0.077	»	»	»
24	N3	C5	6	2.452	10	12	0.094	»	»	»
25	C5	C6	6	2.510	12	12	0.082	»	»	»
26	C1	C5	2	2.695	19	25	0.092	»	»	»
27	N3	H9	12	2.745	14	19	0.224	25	33	ii
28	C5	H11	24	2.789	13	18	0.224	»	»	»
29	N3	N19	1	2.910	20	26	0.085	»	»	»
30	N3	H8	6	3.439	12	18	0.098	5	7	iii
31	C1	C6	4	3.453	17	23	0.117	»	»	»
32	C5	H13	12	3.502	11	13	0.098	»	»	»
33	C1	C20	2	3.759	14	15	0.070	13	13	
34	C1	C21	2	4.191	26	30	0.153	51	57	
35	N3	C20	2	4.305	19	21	0.083	16	14	
36	C1	C22	4	4.641	15	16	0.157	21	24	iv
37	N3	C22	2	4.805	24	25	0.197	»	»	»
38	N3	C21	2	4.905	24	28	0.197	»	»	»
39	N3	C23	2	5.317	24	21	0.260	84	82	
40	C4	C20	1	5.731	24	27	0.085	44	30	
41	C4	C22	2	6.179	37	42	0.320	78	71	v
42	C4	C21	2	6.363	22	24	0.280	»	»	»
43	C6	C22	1	6.417	65	76	0.280	»	»	»
44	C4	C23	2	6.640	24	21	0.280	»	»	»
45	C5	C21	1	6.885	45	54	0.324	»	»	»
46	C6	C23	2	6.925	52	44	0.204	26	18	vi
47	C5	C23	2	7.076	22	24	0.165	»	»	»
48	C5	C22	2	7.104	25	27	0.165	»	»	»
49	C7	C23	1	7.750	35	27	0.110	»	»	»

^{a,b}, See footnotes in Table 1.

realistic *l* values for some important non-bonded distances.

It was also examined whether a mixture of the *anti* form ($\tau = 180^\circ$) together with the *gauche* ($\tau = 65^\circ$) could be present. Geometrical parameters determined for the *gauche* form and only slightly different from those presented in Table 1 were employed in these calculations. Unfortunately, the theoretical distributions were little sensitive to addition of small amounts of the *anti* form. In fact, the agreement improved somewhat with 10 % *anti*, did not change with 20 %, and became somewhat poorer with 30 % (generalized *R*-factor 0.0765, 0.0775, 0.0801 for mixtures with 10, 20, 30 % *anti* vs. 0.0774 for *gauche* only). In these calculations it was assumed that the *anti* form would have the same structure as

the *gauche* form except the torsion angle τ . The *l* values for the rotation-dependent non-bonded distances of the *anti* form were estimated considering the values obtained for the *gauche* form.

Further refinement of some of the *l* values for important non-bonded distances and of some of the bond angles were performed for the mixtures. The results were not very different from those obtained for the *gauche* form only, and depended slightly on the mixture used. It was felt that it would be difficult to give a reliable estimate of the *anti* form content of the mixture. We consider, however, the results obtained for the *gauche* form in a mixture with 20 % *anti* form to be a fair representation of the findings of the present analysis.

Table 1 contains the bond distances, bond and torsion angles and the mean amplitudes of vibration for the bonds. The l values for non-bonded distances of the $\text{C}_3\text{CNCCNCC}_3$ skeleton and distances $\text{C}\cdots\text{H}$ and $\text{N}\cdots\text{H}$ that occur at least six times, are given in Table 2 with indicating typical arrangements of the groups in which these l values were refined. The standard deviations σ_{LS} (and also $\sigma_{\text{LS}}^{\text{corr}}$) given in Tables 1 and 2 refer to a particular refinement scheme in which the parameters for those σ values are given which were allowed to vary simultaneously.* The σ_{LS} values refer to a refinement with unit weights, while the $\sigma_{\text{LS}}^{\text{corr}}$ values were obtained when off-diagonal elements were also included in the weight matrix in order to estimate the influence of correlation between the experimental data on the standard deviations. As for the correlation between the parameters, there were altogether 406 correlation coefficients for the particular refinement scheme for which the results are presented in Tables 1 and 2. Of these coefficients, in order to save space, only those are given in Table 3 whose absolute values are larger than 0.5.

* For the particular scheme the "fudge-factor" was chosen to be nearly zero.

Table 3. Correlation coefficients ρ (associated with the results and corresponding to the notation of Tables 1 and 2) whose absolute value is greater than 0.5.

Parameters 1	2	ρ_{12}^a	$\rho_{12}^{\text{corr}b}$	Parameters 1	2	ρ_{12}^a	$\rho_{12}^{\text{corr}b}$
r2	r3	0.564	0.618	r4	l5	0.789	0.825
r3	r4	0.663	0.692	r5	l5	-0.739	-0.753
r1	r5	-0.624	-0.598	l5	$\alpha 7$		-0.584
r3	r5		-0.546	r1	l(i)	0.688	
r4	r5	-0.682	-0.720	$\alpha 6$	l(i)	-0.753	-0.746
r1	$\alpha 6$	-0.651		$\alpha 7$	l(i)	-0.588	
r1	$\alpha 7$	-0.785	-0.783	$\alpha 9$	l(i)	0.607	0.596
r5	$\alpha 7$	-0.674	-0.704	$\alpha 7$	l34	-0.545	-0.564
$\alpha 6$	$\alpha 7$	0.651		$\alpha 8$	l34	0.554	
r5	$\alpha 8$	0.585	0.613	$\alpha 9$	l34		0.604
$\alpha 7$	$\alpha 8$	0.526	0.558	l(i)	l(ii)	0.704	0.651
$\alpha 6$	$\alpha 9$		-0.526	$\alpha 7$	l21	-0.531	
$\alpha 7$	$\alpha 9$	-0.625	-0.554	$\alpha 9$	l21	0.513	
$\alpha 7$	r11	0.657	0.622	l(i)	l21	0.693	0.594
l2	l3	0.517	0.545	l(ii)	l21		0.553
r3	l5		0.510	s(50) ^c	s(25) ^c	0.520	

^a Refinement scheme with diagonal weight matrix. ^b Refinement scheme with off-diagonal elements also included in the weight matrix. ^c Scale factors for the data sets from the 50 and 25 cm camera ranges, respectively.

DISCUSSION

The bond lengths and bond angles determined for N,N' -di-*t*-butyl-1,2-ethanediimine display no unusual features. A detailed discussion of them, furthermore, would not be justified in the light of the relatively large standard deviations associated with the parameters. Some observations concerning the bond lengths may be of interest, however.

The distance for the central bond $=\text{C}-\text{C}=(1.496(20) \text{ \AA})$ has especially large standard deviation. On the other hand, its value is seen to be rather insensitive to the conditions of refinement applied in various schemes. It is larger than those in 1,2,4,5-hexatetraene ($1.466(4) \text{ \AA}$)⁵ and in 1,3-butadiene ($1.467(3) \text{ \AA}$,⁶ $1.463(3) \text{ \AA}$)⁷. In this connection it is interesting to note that the $=\text{N}-\text{N}=\text{C}$ bond in acetaldazin ($1.437(13) \text{ \AA}$)⁸ is larger than in formaldazin ($1.418(3) \text{ \AA}$)⁹.

The length of the double bond $\text{C}=\text{N}$ in N,N' -di-*t*-butyl-1,2-ethanediimine is nearly the same as in formaldazin ($1.277(2) \text{ \AA}$)⁹ and in acetaldazin ($1.277(3) \text{ \AA}$)⁸.

The most interesting structural feature of the N,N' -di-*t*-butyl-1,2-ethanediimine molecules is their conformational properties. The majority of the molecules in the vapour takes

a *gauche* form with respect to the central bond and this *gauche* form is characterized by a torsion of 65° from the *syn* form. The presence of a smaller amount of the *anti* form is also indicated by the experimental data. The arrangement around the double bonds is *trans*. The conformation around the C-N single bond is such that the C=N double bond and one of the C-C bonds of the adjacent *t*-butyl group are in the same plane.

We are aware of only one previous investigation of the molecular conformation of *N,N'*-di-*t*-butyl-1,2-ethanediimine, viz. that of Exner and Kliegman¹⁰ who suggested a non-planar form on the basis of measurement and calculation of dipole moment. They placed the torsion angle between 90 and 140°, and stressed that the calculations were rather sensitive to the bond angles used. At first sight the present findings seem to be at variance with the conclusions from the dipole moment calculations. However, Exner and Kliegman considered the presence of one conformer only, whereas the dipole moment measurements may be interpreted with a mixture of *anti* form and a *gauche* that is closer to *syn* than to *anti*.

In addition to the *anti* conformer, *gauche* conformers with torsion angles similar to that determined in the present study have been found recently by electron diffraction in several compounds that include oxalyl chloride,¹¹ oxalyl bromide,¹² formaldazin,⁹ acetaldazin.⁸ The relative abundance of *gauche* is larger in oxalyl bromide than in oxalyl chloride, and, in fact, the *gauche* is somewhat prevailing in the bromine derivative at the temperatures applied.¹² A *gauche* form was detected only for hexachloro butadiene [with torsion angle 78.1(1.1)°],¹³ while all 2,3-butadione molecules were found to take the *anti* form.¹⁴

Ab initio calculations performed for 1,2-ethanediimine¹⁵ and formaldazin¹⁶ found a minimum for the *anti* forms only.

The steric requirements of the bulky *t*-butyl groups probably play an important role in establishing the conformational properties of the *N,N'*-di-*t*-butyl-1,2-ethanediimine molecules. They are, however, only one of several competing effects that have to be taken into consideration.

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