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An Electron Diffraction Investigation of the Molecular Structure of Di-*t*-butylnitroxide Free Radical in the Vapour Phase

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The electron diffraction method was used to determine the structure of di-*t*-butylnitroxide radical in the vapour phase. The molecule has symmetry C_2, coplanarity of the nitrogen bonds was assumed. The angular positions of the butyl groups were determined. The additional molecular parameters determined from the experimental radial distribution curves are: C—C $1.53_6 \pm 0.02_0$ Å ($u = 0.05_0$ Å), C—N $1.51_2 \pm 0.02_0$ Å ($u = 0.04_8$ Å), N—O $1.28_0 \pm 0.02_0$ Å ($u = 0.03_0$ Å), C—H $1.10_5 \pm 0.02_0$ Å ($u = 0.07_3$ Å), ∠CNC 136 ± 3°, ∠CCC 107 ± 2° and ∠CCH 110°.

The N—O bond parameters are suggestive of a stable N—O three electron bond.

In 1961 Hoffmann and Henderson[1] reported the discovery of a new group of stable, aliphatic, free radicals, the di-*t*-alkylnitroxides. An example of which was the di-*t*-butylnitroxide radical which they found to be remarkably stable. The stability of the substituted nitroxide radicals known so far could be ascribed to electron delocalization over a conjugated system attached to nitrogen. This cannot explain the stability of the di-*t*-alkylnitroxide radicals since none of the groups bonded to nitrogen are capable of delocalizing the odd electron. Pauling[2] has proposed the existence of stable three electron bonds. Hoffmann and Henderson suggest that the stability of di-*t*-butylnitroxide radical must be explained in terms of a stable N—O three electron bond which leads to a lowered ground state energy.

This electron diffraction investigation of the $[(CH_3)_3C]_2NO$ radical was carried out in order to study the bond arrangement and distances from the nitrogen atom. The sample used in this investigation was kindly placed at our disposal by Dr. A. Kentaro Hoffmann.

EXPERIMENTAL

The electron diffraction diagrams were taken at a temperature of about 70°C. The electron wavelength was 0.064556 Å and a rotating sector with an angular opening proportional to s^3 was used ($s = (4\pi/\lambda) \sin \theta$). The diffraction diagrams were recorded at distances of approximately 48 and 19 cm between the scattering point and the photographic plate, which covered the s-ranges of 1.25—20.00 $Å^{-1}$ and 7.00—40.00 $Å^{-1}$, respectively.

The photometer curves were treated essentially as previously described [3,4] to obtain the intensity curves for the 48 and 19 cm distances. The intensity curves with the final experimental background are shown in Fig. 1. The background was subtracted from the total scattered intensities, and the overlap region of the 48 and 19 cm curves was averaged.

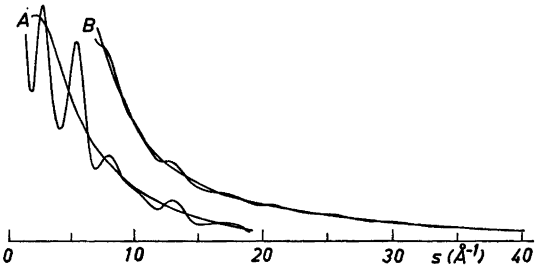

Fig. 1. Di-*t*-butylnitroxide free radical. 48 cm (A) and 19 cm (B) intensity curves with experimental background.

Experimental radial distribution curves were calculated according to the equation

$$\sigma(r)/r = \sum_s I_{obs}(s) \cdot s \cdot [Z_C^2/(Z_C - F_C)^2] \cdot \exp[-ks^2] \cdot \sin(rs)$$

The atomic form factor of carbon used in the s-range $0 < s \leqq 16.00$ $Å^{-1}$, was that of Berghuis *et al.*[5]; extrapolated values were used for $s > 16.00$ $Å^{-1}$. Three different damping constants ($k = 0.0009$, 0.0015, and 0.0036 $Å^2$) were used in the expression $\exp[-ks^2]$.

The lack of intensity data between $0 < s < s_{min}$ was corrected for by subtraction of an experimentally drawn envelope-formed curve from the calculated radial distribution curves.

ANALYSIS OF THE RADIAL DISTRIBUTION CURVES

Fig. 2 shows a radial distribution curve with envelope. The peak complexes at approximately 1.1 and 1.5 Å are due to bond distances. The next three peaks at approximately 2.5, 3.45, and 4.65 Å represent distances between nonbonded atoms. The carbon-nitrogen-oxygen skeleton alone has 36 distances in the r-range between 2.0 and 5.0 Å.

Fig. 3. shows the adopted numbering of the atoms in the molecule. Assuming a planar arrangement around the nitrogen atom, the nine structural parameters can be chosen as the four bond distances: C—C, C—N, N—O, and C—H, the three bond angles: ∠CNC, ∠CCC, and ∠CCH and one angular torsion parameter for each of the butyl groups. Since the bond distances can be determined from the first two peak complexes on the radial distribution curve, the positions of the maxima outside of 2.0 Å are mainly dependent of the five angular parameters.

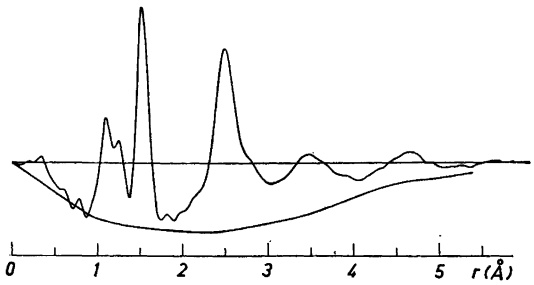

Fig. 2. Di-*t*-butylnitroxide free radical. Radial distribution curve (k = 0.0009 Å^2) with envelope.

Within acceptable limits variations in the angles CCC and CCH cause only small shifts in the positions of the maxima and minima on theoretical curves. A change in the angle CNC and the positions of the methyl groups, however, give significant changes in the distribution of the interatomic distances in the molecule.

The radial distribution curves calculated for a model with free rotation of the butyl groups have no distinct maxima outside of 3.0 Å. The curves calculated for models with the butyl groups fixed in unsymmetrical configurations are also in disagreement with the experimental curve in this region. Exclusion of these models limits the choice of possible structures to two groups:

1) The molecule has the atoms $C_2C_1NC_5$ in the same plane and the butyl groups in the staggered configuration.

2) The molecule has a two-fold axis of symmetry through the nitrogen and oxygen atoms.

This reduces the number of angular torsion parameters to zero and one, respectively. The determination of the structure was accomplished through

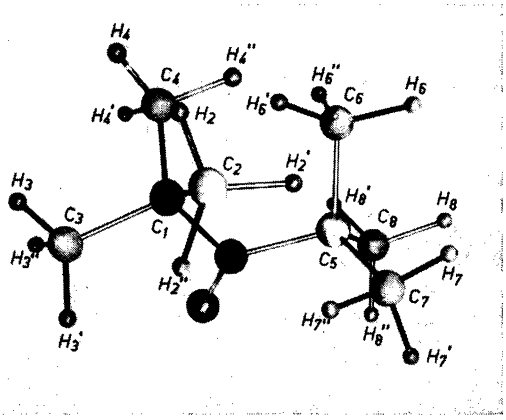

Fig. 3. Numbering of the atoms in the di-*t*-butylnitroxide free radical molecule.

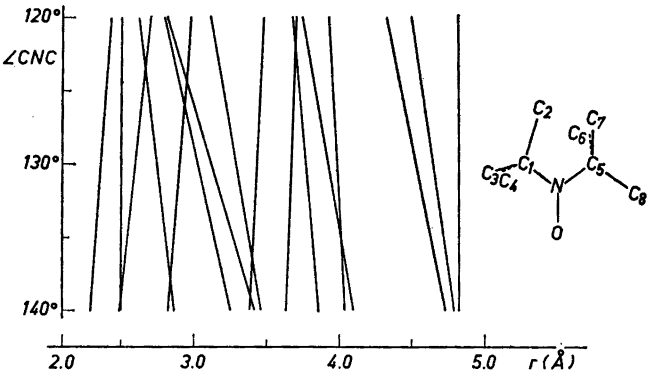

Fig. 4. Di-*t*-butylnitroxide free radical. Variations in the interatomic distances with the angle CNC for a model with the atoms C_2, C_1, N, C_5, and C_8 in the same plane.

an analysis of the variations in the interatomic distances with the remaining angular parameters for each assumption.

The first calculations were based on the carbon-nitrogen-oxygen skeleton only. Fig. 4 shows the interatomic distances as functions of the angle CNC for model 1. The distance contribution on both sides of 3.5 Å is very large, re-

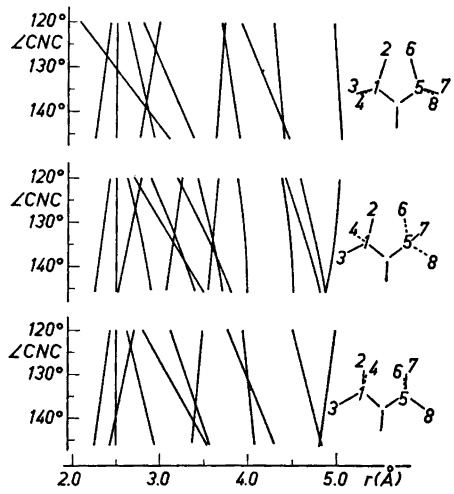

Fig. 5. Di-*t*-butylnitroxide free radical. Variations in the interatomic distances with the angle CNC, for models with a two-fold axis of symmetry.

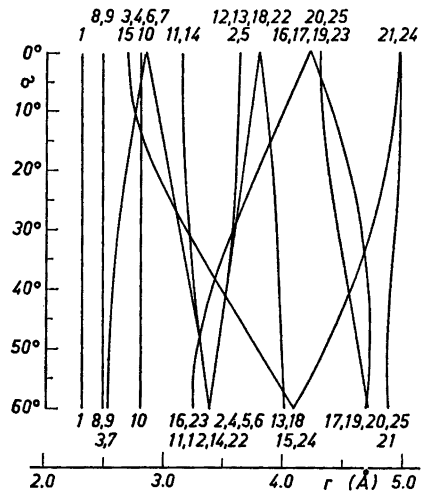

Fig. 6. Di-*t*-butylnitroxide free radical. Variations in the interatomic distances with σ, the angular parameter determining the positions of the methyl groups. σ = 0°, one methyl carbon in each butyl group in *trans* position to the oxygen atom. σ = 60°, one methyl carbon in each butyl group in *cis* position to the oxygen atom.

sulting in two peaks on theoretical radial distribution curves in this region, in disagreement with the experimental curve.

For the model with a two-fold axis of symmetry the distances were first calculated as functions of the angle CNC for three different values of σ, namely 0°, 30°, and 60°; Fig. 5. σ is the angular parameter determining the positions of the methyl groups, defined equal to zero with one methyl carbon in each butyl group in *trans* position to the oxygen atom. The result of a comparison between the diagrams and the experimental radial distribution curve is the following: For $\sigma = 0°$ the distances are not sufficiently concentrated at 3.5 Å and 4.65 Å to be in agreement with the experimental values. For $\sigma = 30°$ and 60° adjustment to the experimental curve can only be obtained for the longest distances in the region about 4.65 Å for ∠CNC approximately 137° and 130°, respectively. No adjustment can be made to the experimental peak at 3.5 Å.

The distances were therefore calculated as functions of the angle σ, for different values of the angle CNC between 130° and 138°. In Fig. 6 the diagram calculated for ∠CNC = 136° is shown. The numbering of the distances in the skeleton is listed in Table 3. A comparison between this distance diagram and the experimental radial distribution curve shows that the σ values between 0° and 40° can be excluded, a good agreement can be obtained for $40° < \sigma < 45°$, while a further increase in σ leads to a new peak at approximately 4.0 Å on the theoretical curve.

The shape of the experimental radial distribution curve at approximately 2.7 Å could not be explained by the carbon-nitrogen-oxygen distances alone. A good agreement was obtained, however, by including the C···H, N···H and O···H distances during the final refinement of the angular parameters.

The shortest H···H distance in the molecule is for all values of σ smaller than the sum of the van der Waals radii for hydrogen which is about 2.5 Å. The region determined for the angle σ gave the largest value for this distance, namely 2.05 — 2.30 Å, depending on the positions of the hydrogen atoms. The shortest H···H distance is either the $H_2'—H_6'$ distance or the $H_4''—H_6'$ and the $H_2'—H_7''$ distances which all become equal when σ is between 42° and 45°. A change in σ leads to decrease in at least one of these distances. The

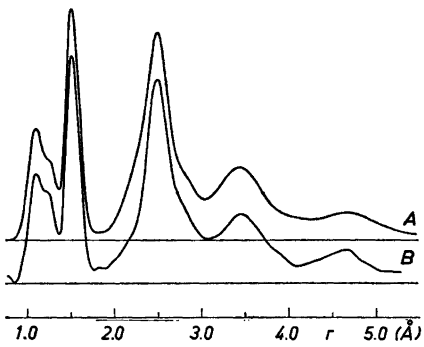

Fig. 7. Di-*t*-butylnitroxide free radical. Theoretical (A) and experimental (B) radial distribution curves (k = 0.0015 Å²).

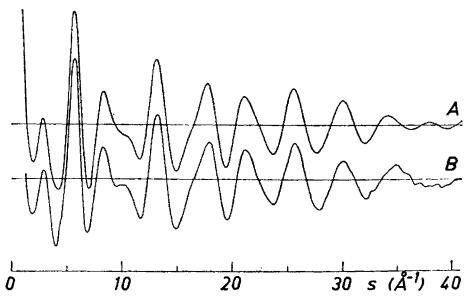

Fig. 8. Di-*t*-butylnitroxide free radical. Theoretical (A) and experimental (B) intensity curves.

equilibrium molecular configuration have thus minimum repulsion between the hydrogen atoms. The shortest oxygen-hydrogen distance was determined to be about 2.43 Å for this configuration.

The determined bond distances and the corresponding u_{ij} values are listed in Tables 1 and 2. The mean values listed in the last column in Table 1 were used for the calculation of the interatomic distances. These distances and the corresponding u_{ij} values determined experimentally are listed in Table 3. Fig. 7 shows a comparison between the experimental and computed radial distribution curves. The correspondence is satisfactory except for some disagreement in the areas under the curves. This is probably due to the difficulty in making accurate determinations of the u_{ij} values for the interatomic distances and the omission of the H···H distances in the computed curve. Fig. 8 shows the experimental and theoretical intensity curves.

Table 1. Experimentally determined bond distances in di-*t*-butylnitroxide free radical (in Å).

Distances	k = 0.0009	k = 0.0015	k = 0.0036	Mean
C–C	1.535	1.535	1.538	1.536
C–N	1.510	1.510	1.515	1.512
N–O	1.275	1.285	1.280	1.280
C–H	1.100	1.105	1.110	1.105

Table 2. Experimentally determined root-mean square deviations from equilibrium internuclear distances (u_{ij} values in Å).

Distances	k = 0.0009	k = 0.0015	k = 0.0036	Mean
C–C	0.050	0.050	0.050	0.050
C–N	0.050	0.050	0.045	0.048
N–O	0.030	0.030	0.030	0.030
C–H	0.075	0.070	0.075	0.073

Table 3. Distances between nonbonded atoms and corresponding u_{ij} values in di-*t*-butylnitroxide free radical (in Å).

Dist.No.	Distance	u_{ij}-value	Atom pair
1	2.318	0.075	$O-C_1$, $O-C_5$
3,7	2.613	0.180	$O-C_3$, $O-C_8$
4,6	3.267	0.180	$O-C_4$, $O-C_7$
2,5	3.546	0.180	$O-C_2$, $O-C_6$
8	2.527	0.080	$N-C_2$, $N-C_3$, $N-C_4$, $N-C_6$, $N-C_7$, $N-C_8$
9	2.467	0.085	C_2-C_3, C_2-C_4, C_3-C_4, C_6-C_7, C_6-C_8, C_7-C_8
10	2.804	0.075	C_1-C_5
11,14	3.310	0.180	C_1-C_6, C_2-C_5
16,23	3.479	0.210	C_2-C_7, C_4-C_6
12,22	3.555	0.180	C_1-C_7, C_4-C_5
15	3.590	0.210	C_2-C_6
13,18	4.005	0.180	C_1-C_8, C_3-C_5
24	4.611	0.210	C_4-C_7
20,25	4.625	0.210	C_3-C_7, C_4-C_8
17,19	4.772	0.210	C_2-C_8, C_3-C_6
21	4.967	0.210	C_3-C_8

Table 3. Continued.

Distance	u_{ij}-value	Atom pair
2.44	0.24	O−H_3'', O−H_8''
2.71	0.24	O−H_3', O−H_8'
3.14	0.24	O−H_4', O−H_7'
3.63	0.24	O−H_2'', O−H_6''
3.70	0.24	O−H_3, O−H_8
3.75	0.24	O−H_4'', O−H_7''
4.00	0.24	O−H_2', O−H_6'
4.18	0.24	O−H_4, O−H_7
4.39	0.24	O−H_2, O−H_6
2.78	0.22	N−H_2', N−H_2'', N−H_3', N−H_3'', N−H_4', N−H_4'', N−H_6', N−H_6'', N−H_7', N−H_7'', N−H_8', N−H_8''
3.48	0.22	N−H_2, N−H_3, N−H_4, N−H_6, N−H_7, N−H_8
2.18	0.11	C_1−H_2, C_1−H_2', C_1−H_2'', C_1−H_3, C_1−H_3', C_1−H_3'', C_1−H_4, C_1−H_4', C_1−H_4'', C_5−H_6, C_5−H_6', C_5−H_6'', C_5−H_7, C_5−H_7', C_5−H_7'', C_5−H_8, C_5−H_8', C_5−H_8''
2.67	0.23	C_2−H_3, C_2−H_4, C_3−H_2, C_3−H_4, C_4−H_2. C_4−H_3 C_6−H_7, C_6−H_8, C_7−H_6, C_7−H_8, C_8−H_6, C_8−H_7
2.72	0.23	C_2−H_3', C_2−H_4'', C_3−H_2'', C_3−H_4', C_4−H_2', C_4−H_3'' C_6−H_7'', C_6−H_8', C_7−H_6', C_7−H_8'', C_8−H_6'', C_8−H_7'
2.81	0.28	C_2−H_7'', C_6−H_4''
2.95	0.28	C_2−H_6', C_6−H_2'
3.08	0.25	C_1−H_6', C_5−H_2'
3.19	0.28	C_4−H_6', C_7−H_2'
3.20	0.28	C_4−H_6'', C_7−H_2''
3.34	0.25	C_1−H_7'', C_5−H_4''
3.44	0.23	C_2−H_3'', C_2−H_4', C_3−H_2', C_3−H_4'', C_4−H_2'', C_4−H_3', C_6−H_7', C_6−H_8'', C_7−H_6'', C_7−H_8', C_8−H_6', C_8−H_7''
3.46	0.25	C_1−H_6'', C_5−H_2''
3.85	0.25	C_1−H_7', C_5−H_4'
3.88	0.28	C_2−H_7', C_6−H_4'
4.06	0.28	C_2−H_6'', C_6−H_2''
4.14	0.25	C_1−H_8', C_5−H_3'
4.28	0.25	C_1−H_8'', C_5−H_3''
4.37	0.25	C_1−H_6', C_5−H_2'
4.42	0.28	C_4−H_7'', C_7−H_4''
4.43	0.28	C_2−H_7', C_6−H_4'
4.44	0.28	C_4−H_8', C_7−H_3'
4.45	0.28	C_3−H_7'', C_8−H_4''
4.51	0.28	C_2−H_6, C_6−H_2
4.56	0.25	C_1−H_7, C_5−H_4
4.57	0.28	C_4−H_6, C_7−H_2
4.60	0.28	C_3−H_7', C_8−H_4'
4.61	0.28	C_3−H_6', C_8−H_2'
4.86	0.28	C_3−H_6'', C_8−H_2''
4.91	0.28	C_1−H_8, C_5−H_3
4.95	0.28	C_3−H_8'', C_8−H_3''
5.05	0.28	C_3−H_8', C_8−H_3'
5.09	0.28	C_2−H_8'', C_6−H_3''
5.13	0.28	C_4−H_7', C_7−H_4'
5.14	0.28	C_4−H_8'', C_7−H_3''
5.15	0.28	C_2−H_8', C_6−H_3'
5.46	0.28	C_4−H_7, C_7−H_4
5.47	0.28	C_4−H_8, C_7−H_3
5.48	0.28	C_2−H_8, C_6−H_3
5.70	0.28	C_3−H_7, C_8−H_4
5.82	0.28	C_3−H_6, C_8−H_2
5.98	0.28	C_3−H_8, C_8−H_3

RESULTS AND CONCLUSION

The following molecular parameters have been determined:

C—C:	$1.53_6 \pm 0.02_0$ Å	u_{CC}:	0.05_0 Å
C—N:	$1.51_2 \pm 0.02_0$ Å	u_{CN}:	0.04_8 Å
N—O:	$1.28_0 \pm 0.02_0$ Å	u_{NO}:	0.03_0 Å
C—H:	$1.10_5 \pm 0.02_0$ Å	u_{CH}:	0.07_3 Å
∠CNC:	$136 \pm 3°$		
∠CCC:	$107 \pm 2°$		
∠CCH:	110° assumed		

The error limits given are not standard deviations but are based on estimates of the precision in the determination.

The molecule has a two-fold axis of symmetry coinciding with the N—O bond. The torsion angle of the butyl groups is determined to be $43 \pm 2°$, the angle is defined equal to zero with one methyl carbon in *trans* position to the oxygen atom. The butyl groups have three-fold axes of symmetry coinciding with the N—C bonds. One hydrogen atom in each methyl group is assumed to be nearest the three-fold axis. The coplanarity of the nitrogen bonds was assumed. A small deviation of the oxygen atom would not be observed because of the complexity of the experimental curves, but there are no reason from the curves to believe in a great deviation.

The stability of substituted nitroxide radicals, R_2NO, can in addition to the formation of a N—O three electron bond be ascribed to electron delocalization over a conjugated system attached to nitrogen if R represents a group capable of delocalizing the odd electron. In that case the bond distances from the nitrogen atom should be shorter than the normal single bond lengths. A crystal structure determination of di-*p*-anisylnitroxide radical by Hansen [6] in 1952 gives 1.23 Å for the NO bond distance and 1.44 Å for the CN bond distance.

Hoffmann and Henderson [1] suggested that the stability of the di-*t*-butylnitroxide radical could be due to a stable N—O three electron bond together with additional stabilization caused by steric inhibition of the N—N and N—O bond formation, preventing the formation of a dimer. Accordingly, only a decrease in the NO bond length should be expected.

The result of this investigation is in agreement with these suggestions. The N—O bond length was determined to be 1.28 Å which is approximately what could be expected for a three electron bond. Pauling [2] gives 1.44 Å as the normal N—O single bond length and 1.20 Å for the N—O double bond length. The N—C bond length was determined to be 1.51 Å which is longer than usually found for the N—C single bond length. We feel that a stretching of these bonds might be caused to avoid a too close H···H contact between the butyl groups. The same reason might explain the value determined for the angle CCC, namely 107°. This angle is normally found larger than the tetrahedral angle in tertiary butyl groups. The equilibrium conformation is determined by the repulsive interaction between H atoms belonging to different butyl groups, giving the largest possible value for the shortest H···H distance. Assuming ∠CCH = 110°, the shortest H···H distance was determined to be about 2.1

Å. Additional stabilization of the molecule might be caused by the close oxygen-hydrogen contact which is about 2.43 Å. The molecule is therefore very crowded and almost spherical preventing the formation of a dimer.

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