June, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 1715—1718 (1982) 1715

Electron Spin Resonance of X-Irradiated Single Crystals of Dicyclohexyldiazene 1,2-Dioxide

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(Received September 11, 1981)

ESR studies of X-irradiated single crystals of dicyclohexyldiazene 1,2-dioxide, $(C_6H_{11}NO)_2$, revealed the generation of the stably trapped radicals $C_6H_{11}N(O)N'H''(O')C_6H_{11}$. The principal elements of the g value were found to be 2.0030, 2.0060, and 2.0086. The principal elements of the hyperfine coupling constants were found to be 3.88, 1.53, and 1.38 mT for N, and 1.53, 1.41, and 1.14 mT for H″. The direction cosines of these principal elements, when compared with those of the bonds in the parent molecule, indicate that the radical is formed by addition of a hydrogen atom to the N=N′ double bond without causing a large change in the molecular framework. The spin densities for this radical were calculated to be 0.041 and 0.47 in the 2s and 2p orbitals of the atom N, respectively.

C-Nitroso compounds in solution produce nitroxide radicals by photochemical or thermal decomposition. It is well established that the radical formation takes place through the nitroso monomer:[1)]

$$(RNO)_2 \underset{\text{or } \Delta}{\overset{h\nu}{\rightleftharpoons}} 2RNO \xrightarrow[\text{or } \Delta]{h\nu} R\cdot + NO\cdot$$

$$+ RNO \longrightarrow R_2NO\cdot + NO\cdot$$

However, little is known about the decomposition of *C*-nitroso compounds in the solid state, where they exist as dimers.

Nitrosocyclohexane has industrial significance as a precursor of cyclohexanone oxime, which is used to give poly(ε-caprolactam). X-Ray analysis revealed that nitrosocyclohexane exists as a dimeric form, dicyclohexyldiazene 1,2-dioxide (**1**), in the crystalline state.[2)] This paper will report the ESR study of X-irradiated single crystals of **1**.

Experimental and Results

Compound **1**, $(C_6H_{11}NO)_2$, mp 117—118 °C, was prepared according to the method of Okamura *et al.*[3)] Single crystals were grown by the slow evaporation of a saturated methanol solution in a refrigerator at 5 °C. The crystals obtained were thin plates (8 mm × 3 mm × 1 mm, Fig. 1) with well developed planes: {100}, {010}, and {001}.

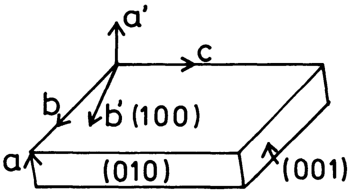

Fig. 1. The crystal form of **1** and the crystallographic axes abc and the rectangular coordinate axes a'b'c employed for analysis of the ESR spectra.

The crystal structure has been determined by Tanimura *et al.* using X-ray methods.[2)] The crystal is triclinic and the space group is $P\bar{1}$ with the unit cell of dimensions: $a_0=1.0133$, $b_0=0.6758$, $c_0=0.5583$ nm, $\alpha=121°42'$, $\beta=96°50'$, $\gamma=78°06'$. The unit cell contains one molecule, which has a center of symmetry at the midpoint of the N=N′ bond.

A rectangular coordinate system a′b′c was chosen for the ESR measurements. The c axis is the same as the crystal c axis. The b′ axis is selected in the bc plane, perpendicular to the c axis, and the a′ axis is perpendicular to the bc plane. The crystal axes were determined by comparing interfacial angles calculated from the lattice constants with those measured with an optical goniometer. The results are shown in Fig. 1.

Single crystals were irradiated with X-rays of 180 keV to a dose of about 1 Mrad (10^4 J/kg) at 77 K. The ESR spectra were measured using a Varian Model V4501 X-band spectrometer.

The ESR spectra measured at 77 K immediately after X-ray irradiation at 77 K were impossible to analyze, since they consisted of a broad, almost featureless

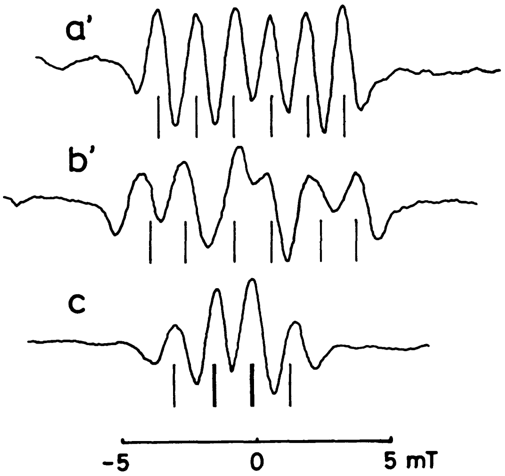

Fig. 2. Second derivative ESR spectra of a single crystal of **1**, which was measured at room temperature after X-Rays irradiation at 77 K. The magnetic filed was applied parallel to the a′, b′, or c axis, and measured relative to the reference DPPH signal ($g=2.0036$).

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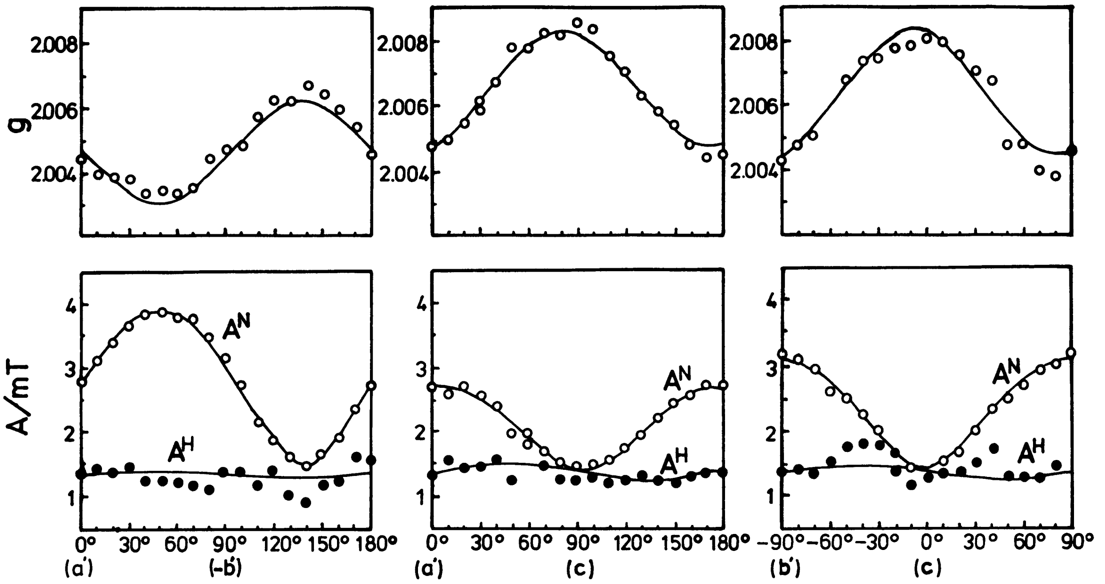


Fig. 3. Angular dependencies of A^N, A^H, and g in an X-irradiated single crystal of **1**. The magnetic field is in the a′b′, a′c, and b′c planes. The circles indicate the observed values and the solid lines indicate the theoretical curves.

Table 1. The principal values of g, A^N, and A^H and their direction cosines with regard to the a′b′c system

g, A^N, and A^H	Principal values	Direction cosines with regard to the a′b′c system		
g_1	2.0030	0.670	−0.743	0.018
g_2	2.0060	0.709	0.631	−0.314
g_3	2.0086	0.222	0.223	0.949
$A_1{}^N$/mT	3.88	0.643	−0.765	0.023
$A_2{}^N$/mT	1.53	0.659	0.569	0.492
$A_3{}^N$/mT	1.38	0.389	0.301	−0.871
$A_1{}^H$/mT	1.53	0.539	0.309	0.784
$A_2{}^H$/mT	1.41	0.639	−0.756	−0.141
$A_3{}^H$/mT	1.14	0.549	0.577	−0.605

absorption. However, the spectra measured at room temperature became simple after storage at room temperature. Some typical spectra are shown in Fig. 2. Each spectrum, consisting of six lines with equal intensity, can be interpreted in terms of one anisotropic nitrogen hyperfine coupling constant A^N and one nearly isotropic proton hyperfine coupling constant A^H. Each component line is broad, having about 0.7 mT of maximum slope width.

The observed angular dependencies of A^N, A^H, and g values are plotted in Fig. 3. Principal elements of A^N-, A^H-, and g-tensors are determined using the least-squares method and are given in Table 1. The solid lines in Fig. 3 are the theoretical angular variations calculated from the principal elements in Table 1.

Discussion

The observed coupling constants clearly show that the free radical contains a nitrogen atom having a large fraction of unpaired electrons and β-type hydrogen atom with nearly isotropic coupling constant. Table 1 shows that the nitrogen coupling tensor has almost cylindrical symmetry about the $A_1{}^N$ direction. This symmetry is to be expected for the unpaired electron in a nitrogen orbital aligned in this direction when the contribution from unpaired electrons on other orbitals is negligible. The analysis of coupling tensors of this type has been fully discussed in a previous paper.[4] The results are summarized as follows.

The molecular orbital containing the unpaired electron can be written as

$$\phi = C_s\phi_{2s}{}^N + C_p\phi_{2p}{}^N + C_h\phi_{1s}{}^H \; C_x\phi^X,$$

where $\phi_{2s}{}^N$, $\phi_{2p}{}^N$, and $\phi_{1s}{}^H$ are the 2s, 2p atomic orbitals of the nitrogen atom and the 1s atomic orbital of the hydrogen atom, respectively, and ϕ^X is a normalized orbital of a group of atoms that makes negligible contribution to the hyperfine structure. Coefficients are obtained from the relations:

$$C_s{}^2 = a^N/A_{2s}{}^N,$$
$$C_p{}^2 = (A_1{}^N - a^N)/(2B_{2p}{}^N),$$
$$C_h{}^2 = a^H/A_{1s}{}^H,$$
$$C_x{}^2 = 1 - C_s{}^2 - C_p{}^2 - C_h{}^2,$$

where

$$a^N = (A_1{}^N + A_2{}^N + A_3{}^N)/3,$$
$$a^H = (A_1{}^H + A_2{}^H + A_3{}^H)/3.$$

The 2p orbital is parallel to the direction of $A_1{}^N$(maximum) and g_1(minimum).

With the observed values in Table 1 and $A_{2s}{}^N$=55.0 mT, $B_{2p}{}^N$=1.71 mT, and $A_{1s}{}^H$=50.8 mT,[5] one finds $C_s{}^2$=0.041, $C_p{}^2$=0.47, $C_h{}^2$=0.027, and $C_x{}^2$=0.462; the total spin density on the nitrogen atom is 0.51. The directions of g_1 and $A_1{}^N$ are calculated to be 1.6° apart; they are parallel within the experimental error.

The spin densities and g values of this radical are compared in Table 2 with those of nitroxide and iminoxyl radicals, which are typical π- and σ-radicals, respectively. The comparison suggests that this radical

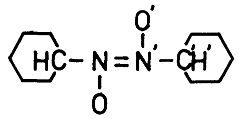
TABLE 2. SPIN DENSITIES AND g FACTORS OF RADICALS CONTAINING N–O GROUP

	Nitroxyl radical[a,b]	The radical in this work	Iminoxyl radical[c]
C_s^2	0.027	0.041	0.050
C_p^2	0.50	0.47	0.36
g_1	2.0027	2.0030	2.0025
g_2	2.0061	2.0060	2.0064
g_3	2.0089	2.0086	2.0118

a) Ref. 7. b) The isotropic proton coupling constant of dimethyl nitroxide radical was 1.23 mT: J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966). c) Ref. 4.

has an electronic structure similar to that of nitroxide radical except for the high spin density on the 2s atomic orbital of the nitrogen atom.

Stable radicals trapped in irradiated organic crystals at room temperature include the following types: (1) The primary free radicals formed by dissociation of the undamaged molecules; (2) the secondary free radicals formed by addition of the primary radicals of small size to the undamaged molecule or to diamagnetic molecular fragments that are produced by the dissociation of the undamaged molecules. There are seven possible radicals (**2**—**8**) of this type that can be produced from **1** and have a coupling nitrogen atom with the spin density of about one half. All the radicals except **2** will be readily excluded from the canditates for the observed radical since these radicals cannot be reconciled with the observed coupling constants.



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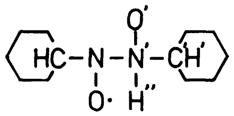

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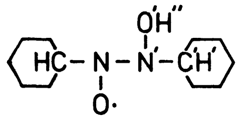

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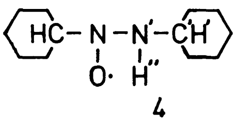

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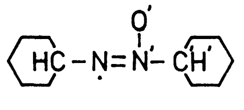

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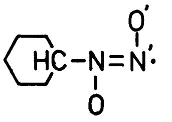

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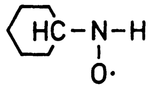

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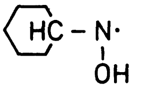

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Radical **7** has an anisotropic coupling proton of the NH group. The anisotropy of the coupling constant, $A_{\max}^H - A_{\min}^H$, for an α proton of an $\dot{>}$N–H π radical is proportional to the spin density on the nitrogen 2p orbital (ρ_π^N) with a proportional constant of 3.2 mT.[6] With the spin density of 0.47, the anisotropy in **7** is estimated to be 1.5 mT; this is different from the observed anisotropy of 0.39 mT. It is shown in the same way that the proton coupling of the OH group of **8** has an anisotropy different from the observed one. Thus **7** and **8** are excluded.

Radicals **5** and **6** probably give rise to two discernible couplings due to N and N′ atoms, because spin densities on these atoms do not seem to differ too much. Because only one nitrogen coupling was observed, **5** and **6** can be excluded.

Radicals **2**, **3**, and **4** can be formed from the parent molecule as a result of hydrogen addition or hydrogen addition after oxygen abstraction. Therefore, it can be assumed that all atoms in these radicals except O′ and H″ occupy the same positions in the lattice as those in the parent molecule. The isotropic coupling constant of H, a^H(CH), can be expressed by McConnell's $\cos^2\theta$ rule:

$$a^H(CH) = Q_N^{CH} \rho_\pi^N \cos^2\theta,$$

where θ is a dihedral angle between the C–H bond in the parent molecule and the unpaired electron orbital (parallel to A_1^N and g_1) in the observed radical, and $\rho_\pi^N = (C_{2p}^N)^2$. The orientation of the parent molecule in the crystal, determined by X-ray analysis, is given in Table 3. Using the value of 76—77° for θ calculated from Tables 1 and 3, 0.47 for ρ_π^N from Table 2, and 5.0 mT for Q_N^{CH}, one obtains 0.2 mT for a^H(CH). Because this value is much smaller than the observed isotropic proton coupling of 1.36 mT, the observed one is not attributable to the hydrogen atom of the CH group.

TABLE 3. ORIENTATION OF THE PARENT MOLECULE WITH REGARD TO THE a′b′c SYSTEM

Bond and normal	Direction cosines with regard to the a′b′c system		
	a′	b′	c
C–H	−0.445	−0.151	−0.882
N–C	0.551	0.379	−0.743
N–O	0.164	0.256	0.952
N–N′	−0.720	−0.655	−0.228
n_1[a]	0.478	−0.874	−0.091
n_2[b]	0.646	−0.758	0.093

a) n_1: The normal to the plane HCN of **1**. *b*) n_2: The normal to the plane CNO of **1**.

The ESR of *t*-butyl cyclohexylamino nitroxide analogous to **4**, has been studied in solution; its isotropic couplings were 1.86 mT for N(NO), 0.09 mT for N(NH), H(CH), and H(NH).[8] The isotropic coupling constant of H(NH) of **4** is probably close to 0.09 mT; this value cannot account for the observed value of 1.36 mT. In nitroxide radicals, the unpaired electron is mainly localized on the >N–O moiety; hence the proton coupling constant of H(OH) in **3** will be too small to explain the observed constant. Thus there remains only **2** as a candidate. The following discussion will show that **2** is consistent with the ESR data of the trapped radical.

In the parent molecule **1**, six atoms CNOC′N′O′ are almost planar and oxygen atoms are placed *trans* with regard to the N=N′ bond. Radical **2** is produced by the rupture of this π bond with the addition of H″ at N′. For the time being, we shall assumed that CNON′ in **2** occupies the same position in the lattice as in the parent molecule. Then, the unpaired electron occupies a molecular orbital composed of the p_π orbitals of N and O, which are perpendicular to the CNO plane. This can explain the result that the normal to the CNO plane was calculated from the direction cosines in Tables 1 and 3 to make an angle of 4° with the directions of g_1 and A_1^N, therefore with the direction of the p_π orbital. On addition of H″ to N′, the hybridization of the nitrogen orbitals changes from sp^2 to sp^3. Then O′ is moved and N′–H″ uses one of the sp^3 hybrid orbitals, making a dihedral angle of 30° with the p_π orbital of the unpaired electron. Though nitroxide radicals with –N(O·)NH(O)– moiety have not been reported, a radical $H\dot{N}-NH_3^+$ somewhat analogous to **2** was reported by Shrivastava and Anderson[9] and extensively discussed by Gordy.[6] The resultant parameters are $a^N(NH_3)=0.4$ mT, $a^H(NH_3)=1.50$ mT, $\rho_\pi^N=0.97$, $Q_N^{NH}=3.09$ mT, where Q_N^{NH} is the coefficient in

$$a^H(NH_3) = Q_N^{NH}\rho_\pi \cos^2\theta.$$

Applying this relation to **2** with $\rho_\pi^N=0.47$ and $\theta=30°$, we obtain 1.09 mT for the coupling constant of H″, which agrees well with the observed one of 1.36 mT.

The hydrogen atom H″ added at N′ will occupy two positions in the lattice; one lies above the NN′C′ plane, the other below the plane. The anisotropic coupling tensor of each hydrogen atom is calculated and compared with the observed coupling tensor of A^H. The position of H″ was not determined with assurance because of the relatively large angular error in the observed coupling tensor.

The coupling of β-nitrogen is supposed to be proportional to the spin density on the α-nitrogen. The coupling constant of 0.4 mT for $\rho_\pi^N=0.97$ in $HN-NH_3^+$ predicts that of **2** to be about 0.2 mT from $\rho_\pi^N=0.47$. This is within the observed line width of 0.7 mT.

If the nitroxide moiety of **2** is perfectly planar, it will have the spin density on the nitrogen 2s orbital approximately equal to that of ordinary nitroxide radicals. However, Table 2 shows that the former (0.041) is appreciably larger than the latter (0.027). The difference suggests a change of nitroxide moiety from planar configuration. Experimental and theoretical studies have shown that the methyl radical is planar and the radicals CF_3, CHF_2, and CH_2F are pyramidal.[10,11] Pauling has shown by a simple quantum-mechanical argument that the electronegativity difference of the atom is the major factor in determining the configuration of these radicals.[11] For a radical $\dot{M}X_3$, as X is more electronegative than M, the unpaired electron orbital will contain more charactor of M and the radical will have a pyramidal structure. This explains the configuration change in nitroxide radicals: If one replaces an alkyl group in the dialkyl nitroxide radical with a nitrogen function, the spin density on the nitrogen 2s orbital of the nitroxide moiety will increase.

We therefore conclude that the radical stably trapped in the solid state is **2**.

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