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Perchlorodiphenylnitroxide, a Free Radical

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Abstract. $(C_6Cl_5)_2NO\cdot$, $M_r = 528.62$, $F(000) = 1028$, monoclinic, $C2/c$, $a = 16.652$ (7), $b = 5.284$ (2), $c = 19.304$ (8) Å, $\beta = 90.84$ (3)°, $V = 1698.73$ Å^3, $Z = 4$, $D_c = 2.066$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.7107$ Å, $\mu = 16.3$ cm^{-1}. The structure has been solved with *MULTAN* and refined by the block-diagonal least-squares method. The final R value is 0.046 for 1964 observed reflexions. The two parts of the molecule are related by a twofold axis passing through the N and O atoms. The perchlorophenyl group and the $C_2NO\cdot$ group are both planar. The dihedral angle between these two planes is 57.2°.

Introduction. Red prismatic crystals of perchlorodiphenylnitroxide were kindly supplied by Professor M. Ballester. They were obtained by crystallization in benzene and washed with pentane.

A crystal, $0.2 \times 0.3 \times 0.4$ mm, was used for crystal data and intensity measurements on a Nonius CAD-4 diffractometer. The unit cell was measured by automatically centring 25 independent reflexions and refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Mo $K\alpha$ radiation, monochromatized by reflexion from a graphite crystal, at a take-off angle of 5°. The ω–2θ technique was used with scan interval $\Delta\omega = (0.70 + 0.35 \tan \theta)°$. The background was measured before and after each reflexion. The maximum scan time was 80 s, with 53.3 s used for the peak scanning and 13.3 s for both backgrounds. The intensity of 133 was chosen as the standard and it was measured every hour. The reflexions $2,2,\overline{12}$, $3,1,\overline{15}$ and $31\overline{3}$, chosen as an orientation control, were measured every 100 reflexions. 2537 independent reflexions were collected within the range $1 < \theta \le 30°$, 1964 of which have been considered as observed, applying the condition $I > 2\sigma(I)$. The data were collected with the crystal mounted along the long axis. Lorentz–polarization corrections were made, but none were for absorption ($\mu r < 0.7$).

The observed systematic absences indicated that the possible space groups are $C2/c$ (centrosymmetric) and Cc (non-centrosymmetric). The statistical results of $\langle ||E|^2 - 1| \rangle$, $\langle |E| \rangle$, and the $N(z)$ distribution (Howells, Phillips & Rogers, 1950) indicated that the space group is $C2/c$.

The structure was solved with the *MULTAN* system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The overall temperature factor was 3.8 Å^2. 274 reflexions with $|E| \ge 1.61$ were used in the phase-determining procedure, because at this value the experimental $N(z)$ (Howells, Phillips & Rogers, 1950) coincides with the theoretical value in centrosymmetric crystals (Solans, 1977). 2000 Σ_2 relationships were used and an E map computed with the phases from the set with the highest combined figure of merit ($= 3$) revealed peaks for all the atoms.

The structure was isotropically and anisotropically refined by means of block-diagonal least squares with the modified version of *SFLS* (Ahmed, Hall, Pippy &

Huber, 1966) written by Solans. The function mini-
mized was $w\|F_o\| - |F_c|^2$, where $w = (3 + |F_o| + 0.02|F_o|^2)^{-1}$. The refinement was terminated at $R = 0.046$ for all observed reflexions where R is defined as $\sum\|F_o\| - |F_c\|/\sum|F_o|$. The scattering factors were from Forsyth & Wells (1959). The final atomic parameters are listed in Table 1. Fig. 1 shows a view of the molecule and the numbering of the atoms, drawn by the ORTEP program (Johnson, 1965). The molecular-geometry calculations were performed with the computer program CGMC (Solans & Font-Altaba, 1975).* The bond distances and angles are shown in Fig. 2.

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* Lists of structure factors, anisotropic thermal parameters, and the equation of the benzene least-squares plane and distances of atoms from the plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33428 (13 pp.). Copies may be obtained through The Executive Secretary, International Union Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic parameters* $(\times 10^5)$, *with estimated standard deviations in parentheses*

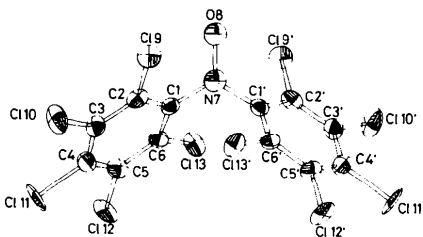|	x	y	z
C(1)	46524 (17)	25229 (52)	19271 (14)
C(2)	38488 (18)	29124 (57)	17327 (15)
C(3)	35050 (18)	14467 (64)	12046 (16)
C(4)	39646 (18)	−3967 (61)	8747 (16)
C(5)	47695 (18)	−6912 (57)	10467 (15)
C(6)	51135 (16)	8032 (53)	15620 (14)
N(7)	50000 (0)	38816 (84)	25000 (0)
O(8)	50000 (0)	62902 (70)	25000 (0)
Cl(9)	32707 (5)	51132 (18)	21476 (4)
Cl(10)	25099 (5)	17927 (23)	9890 (5)
Cl(11)	35285 (5)	−22577 (20)	2443 (5)
Cl(12)	53314 (5)	−29243 (17)	6290 (4)
Cl(13)	61246 (4)	5683 (17)	17243 (4)

Fig. 1. View of the molecule drawn by the ORTEP program, showing thermal ellipsoids and the numbering of the atoms.
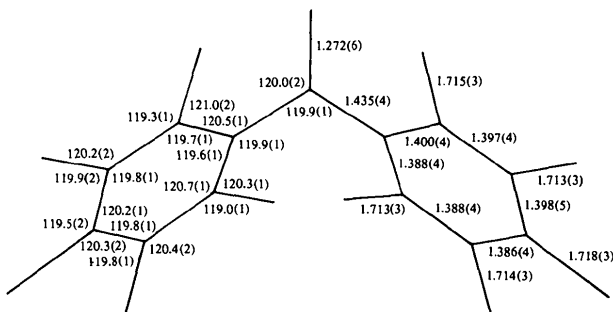

Fig. 2. Bond distances (Å) (right) and bond angles (°) (left).

Discussion. This compound was synthesized by Ballester, Riera & Onrubia (1976). They found that this shielded radical is more inert and more stable than other diarylnitroxide free radicals.

The bond distances and angles between the atoms of the $C_2NO\cdot$ group are similar to those obtained by Hanson (1953) in dianisylnitroxide. Moreover, the distance N(7)—O(8) is close to the values obtained in other nitroxide free radicals, as in 2,2,6,6-tetra-methylpiperidin-4-ol-1-oxyl (Lajzérowicz-Bonneteau, 1968), and di-*tert*-butylnitroxide (Andersen & Andersen, 1966).

The benzene ring is nearly planar [the largest distance atom—mean plane is 0.029 (3) Å]. The C—C (mean distance $= 1.391$ Å), C—Cl (1.715 Å), and Cl—Cl (3.097 Å) distances, and the C—C—C (120.0°), and C—C—Cl (120.0°) angles in the perchlorophenyl group are typical values for a benzene system, as in hexachlorobenzene (Brown & Strydom, 1974), or in decachlorobiphenyl (Pedersen, 1975; Gali, 1975). The dihedral angle between the two benzene rings is 87.4°, which is greater than the value of 72° obtained by Silverman, Soltzberg, Yannoni & Krukonis (1971) in the perchlorodiphenylmethyl stable free radical.

The torsion of the C(1)—N(7) bond (57.5°) is due to steric hindrance between Cl(13), Cl(19), N(7) and O(8) (Tables 2 and 3). According to the double-quartet theory of Linnett (1961), the torsion angle C(1)—N(7) explains the high stability of this compound, because it forces the perchlorophenyl groups almost completely out of conjugation with the N—O· group; the unpaired electron density is thus located practically in the N—O· group. [The non-stability of the diarylnitroxides is due to unpaired electron delocalization in the phenyl groups (Forrester, Hay & Thomson, 1968).]

C(1), N(7), O(8) and C(1′) are required by symmetry to be coplanar, therefore the angle α between the N—O bond and the C—N—C plane is 0°, as in the structures reported by Hanson (1953) and Andersen & Andersen (1966). These results do not agree with the conclusion of Kochi (1972), who has discussed the degree of non-planarity of the $C_2NO\cdot$ group in terms of this angle α, and concluded that these radicals have an α of about 30°.

Table 2. *Selected intramolecular distances* (Å)

Cl(13)—Cl(9′)	3.385 (1)	N(7)—Cl(13)	2.983 (3)
O(8)—Cl(9)	3.015 (1)	C(1)—Cl(13′)	3.100 (3)
N(7)—Cl(9)	3.022 (1)		

Table 3. *Selected torsion angles* (°)

C(2)—C(1)—N(7)—O(8)	57.5 (3)
C(2)—C(1)—N(7)—C(1′)	−122.5 (3)
C(6)—C(1)—N(7)—O(8)	−122.6 (2)
C(6)—C(1)—N(7)—C(1′)	57.3 (3)
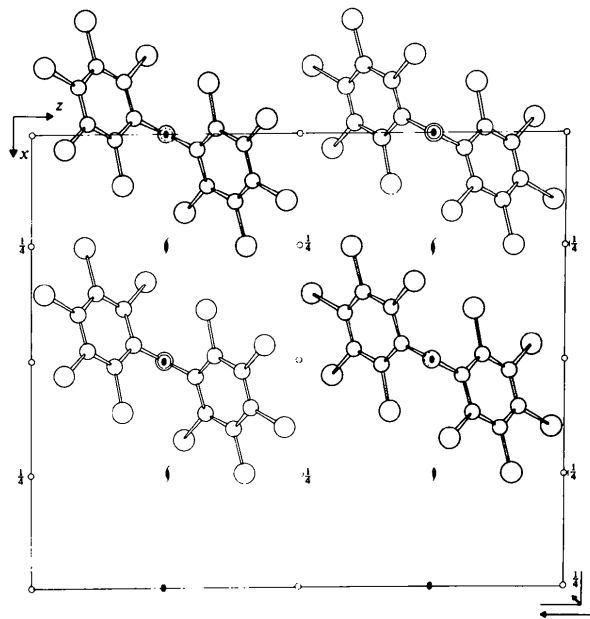
Fig. 3. A projection of the unit-cell contents down *b*.

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Fig. 3 is a projection of the crystal structure down *b*. The molecules are packed in layers along the *xz* plane.

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A 1:1 Complex of Theophylline and *p*-Nitrophenol

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Abstract. $(C_7H_8N_4O_2)(C_6H_5NO_3)$, triclinic, $P\bar{1}$, $a = 8.29$ (2), $b = 11.56$ (3), $c = 8.95$ (2) Å, $\alpha = 114.0$ (2), $\beta = 108.9$ (2), $\gamma = 75.4$ (2)°, $Z = 2$. Block-diagonal least-squares refinement gave a final R value of 0.095. The theophylline molecules are in a dimeric arrangement by virtue of two centrosymmetrically related

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