

tions, there are no simple crystal-packing arguments for the observed preference of the *exo-endo* conformation.

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A Charge-Transfer Complex of Benzene with a Highly Twisted Perylene Derivative

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Abstract. $2C_6H_6 \cdot C_{26}H_6Cl_8N_2O_4$, benzene–1,2,5,6,7,8,11,12-octachloro-*N,N'*-dimethylperylene-3,4:9,10-bis(dicarboximide) (Cl_8DMP) (2/1), $M_r = 850.20$, orthorhombic, $Pna2_1$, $a = 23.076$ (2), $b = 7.2492$ (6), $c = 20.277$ (2) Å, $V = 3392.0$ (8) Å³, $Z = 4$, $D_m = 1.69$ (1), $D_x = 1.665$ g cm⁻³, $\mu(Mo K\alpha, \lambda = 0.71073 \text{ \AA}) = 7.1$ cm⁻¹, $F(000) = 1712$, $T = 297$ (1) K, $R_F = 0.061$ for 2134 observed reflections. The structure contains alternating benzene and Cl_8DMP molecules stacked along **b** to form a 2:1 donor–acceptor complex. The Cl_8DMP molecule is highly twisted as a result of short intramolecular bay $Cl \cdots Cl$ contacts [3.109 (3), 3.136 (3) Å]. The central ring of the perylene fragment is substantially distorted from planarity; internal torsion angles range from 16 (1) to 32 (1)°.

Introduction. The highly chlorinated derivative of perylene, Cl_8DMP , was prepared as part of an effort to synthesize and examine a series of electron acceptors as candidates for incorporation in solar photovoltaic cells (Panayotatos, Parikh, Sauers, Bird, Piechowski & Husain, 1986) designed to work in the *p-n* mode with a compatible pair of stable solid organic dyes. The unchlorinated perylene diimide is a well known commercial dye and an

efficient photoconductor (Popovic, Loutfy & Hor, 1985), but lacks strong electron affinity. It is also an exceedingly insoluble seven-ring aromatic molecule. Cl_8DMP has greater electron affinity and is soluble in a variety of organic solvents. Crystallization from a solution of Cl_8DMP in benzene yielded a 2:1 benzene– Cl_8DMP complex whose structure we report here.

Experimental. Cl_8DMP was prepared by reacting commercially obtained *N,N'*-dimethylperylene-3,4:9,10-bis(dicarboximide) at 333 K with chlorosulfonic acid and excess chlorine; iodine was used as a catalyst. Mass-spectral analysis of the reaction product indicated the presence of hexachloro, heptachloro, and octachloro derivatives which were separated by column chromatography (silica-gel column, benzene eluent). Diffraction-quality crystals were grown by evaporation from benzene.

Structure solution: D_m by flotation; dark-red prism 0.25 × 0.35 × 0.45 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated $Mo K\alpha$ radiation; θ – 2θ scan. Reciprocal-lattice symmetry and systematic absences ($0kl, k + l = 2n + 1; h0l, h = 2n + 1$) consistent with space group $Pna2_1$. Cell constants from setting angles of 25 reflections with $13.40 < \theta < 18.26^\circ$; data corrected for Lorentz, polarization and absorption (empirical correction, ψ scan; $0.95 < T < 1.00$) effects. Variation in intensity

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of three standard reflections $\pm 0.7\%$; 2570 unique reflections measured with $4 < 2\theta < 45^\circ$; 2134 with $I > \sigma(I)$ used in refinement. Data collected: $h\ 0 \rightarrow 24$, $k\ 0 \rightarrow 7$, $l\ 0 \rightarrow 21$. Structure solved by direct methods (*MULTAN82*: Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms from difference maps and at calculated positions; C—H distance = 0.95 Å; B_H set to 1.3 B_N before final refinement cycles; H atoms not refined. Full-matrix least-squares refinement on F ; all Cl₈DMP atoms anisotropic; benzene C atoms isotropic; $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$. Final $R_F = 0.061$, $wR = 0.080$, $S = 2.84$, $(\Delta/\sigma)_{\max} < 0.09$, $\Delta\rho_{\max} = 0.56\text{ e \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974); programs from Enraf-Nonius (1985) *SDP*.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* A view of the Cl₈DMP molecule, showing the atom-numbering scheme, is given in Fig. 1. Selected bond distances and angles are listed in Table 2. A partial view of the structure, showing the stacking of benzene and Cl₈DMP molecules, is given in Fig. 2.

The structure contains alternating Cl₈DMP and benzene molecules stacked along the *b* direction to form a 2:1 benzene—Cl₈DMP donor—acceptor complex. One benzene molecule is associated with rings *B*, *C* and *F* of Cl₈DMP, while the other benzene molecule is associated with rings *D*, *E* and *G*. As judged by the closest C(benzene)⋯C(Cl₈DMP) intermolecular contacts, which for the 12 C(benzene) atoms range from 3.38 (1) to 3.66 (2) Å, each benzene molecule overlaps equally well with the Cl₈DMP molecules above and below it along the stack direction. The shortest intermolecular contacts are comparable to those found in related complexes such as the 1:1 complex of perylene and 7,7,8,8-tetracyanoquinodimethane [3.39 Å (Tickle & Prout, 1973)] and the 1:1 complex of perylene and 2,5-dibromo-3,6-dichloro-*p*-benzoquinone [3.37 Å (Kozawa & Uchida, 1979)]. The benzene rings are planar to ± 0.023 Å. However, the Cl₈DMP molecule is highly twisted, as indicated by the dihedral angle of 35.53 (9)° between the least-squares planes for rings *BCF* and *DEG*. Similar dihedral angles [35.1 (2) and 35.8 (1)°] are observed between planes *F* and *G*, and *BC* and *DE*, respectively. Examination of these dihedral angles as well as torsion angles reveals

Table 1. Fractional atomic coordinates and isotropic thermal parameters

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / <i>B</i> _{eq} (Å ²)
Cl(1)	0.0614 (1)	0.1156 (4)	1.000	4.15 (5)
Cl(2)	0.1724 (1)	0.1255 (5)	1.0792 (2)	5.71 (7)
Cl(5)	0.3296 (1)	0.5320 (6)	0.7639 (2)	7.09 (9)
Cl(6)	0.2173 (1)	0.5207 (4)	0.6926 (1)	4.11 (5)
Cl(7)	0.1673 (1)	0.1328 (4)	0.6605 (1)	4.15 (5)
Cl(8)	0.0556 (1)	0.1893 (5)	0.5839 (1)	6.00 (7)
Cl(11)	-0.0826 (1)	0.6112 (6)	0.9055 (2)	6.83 (8)
Cl(12)	0.0264 (1)	0.5293 (4)	0.9785 (1)	3.65 (5)
O(1)	0.2862 (3)	0.230 (1)	1.0646 (3)	5.8 (2)
O(2)	0.3786 (3)	0.391 (1)	0.8778 (4)	4.9 (2)
O(3)	-0.0562 (3)	0.291 (1)	0.6062 (3)	5.4 (2)
O(4)	-0.1392 (3)	0.479 (1)	0.7949 (4)	5.2 (2)
N(1)	0.3313 (3)	0.300 (1)	0.9692 (4)	3.6 (2)
N(2)	-0.0964 (3)	0.385 (1)	0.7016 (4)	3.7 (2)
C(1)	0.1215 (4)	0.215 (1)	0.9657 (4)	2.6 (2)
C(2)	0.1754 (4)	0.202 (1)	0.9995 (4)	3.4 (2)
C(3)	0.2263 (4)	0.255 (1)	0.9692 (4)	2.7 (2)
C(4)	0.2758 (4)	0.361 (1)	0.8691 (5)	2.8 (2)
C(5)	0.2730 (4)	0.428 (1)	0.8045 (5)	3.2 (2)
C(6)	0.2192 (3)	0.415 (1)	0.7704 (4)	2.7 (2)
C(7)	0.1095 (4)	0.241 (1)	0.7000 (4)	2.7 (2)
C(8)	0.0562 (4)	0.246 (1)	0.6675 (4)	2.9 (2)
C(9)	0.0074 (4)	0.309 (1)	0.6983 (4)	2.7 (2)
C(10)	-0.0396 (4)	0.417 (1)	0.8021 (4)	2.6 (2)
C(11)	-0.0324 (4)	0.476 (1)	0.8651 (4)	2.9 (2)
C(12)	0.0195 (4)	0.442 (1)	0.8993 (4)	2.5 (2)
C(13)	0.0663 (4)	0.354 (1)	0.8700 (4)	2.3 (2)
C(14)	0.1193 (3)	0.293 (1)	0.9025 (4)	1.8 (2)
C(15)	0.1724 (4)	0.311 (1)	0.8671 (4)	2.3 (2)
C(16)	0.1711 (3)	0.342 (1)	0.7990 (4)	2.3 (2)
C(17)	0.1155 (3)	0.304 (1)	0.7633 (4)	2.4 (2)
C(18)	0.0642 (3)	0.337 (1)	0.7991 (4)	2.0 (2)
C(19)	0.0098 (3)	0.352 (1)	0.7671 (4)	2.6 (2)
C(20)	0.2250 (3)	0.307 (1)	0.9000 (4)	2.3 (2)
C(21)	0.2822 (4)	0.261 (1)	1.0062 (5)	3.8 (2)
C(22)	0.3330 (4)	0.354 (1)	0.9030 (5)	3.8 (2)
C(23)	-0.0487 (4)	0.327 (1)	0.6637 (5)	3.5 (2)
C(24)	-0.0952 (4)	0.429 (1)	0.7677 (5)	3.5 (2)
C(25)	0.3866 (4)	0.296 (2)	1.0079 (6)	5.7 (3)
C(26)	-0.1524 (4)	0.397 (2)	0.6678 (6)	5.5 (3)
C(27)	0.2656 (5)	0.228 (2)	0.5063 (6)	4.6 (2)*
C(28)	0.2198 (5)	0.276 (2)	0.4706 (6)	5.7 (3)*
C(29)	0.2328 (5)	0.330 (2)	0.3987 (7)	6.2 (3)*
C(30)	0.2882 (5)	0.326 (2)	0.3782 (6)	5.1 (2)*
C(31)	0.3300 (5)	0.266 (2)	0.4192 (6)	4.5 (2)*
C(32)	0.3208 (5)	0.220 (2)	0.4805 (6)	4.6 (2)*
C(33)	0.4241 (5)	0.295 (2)	0.2535 (6)	5.4 (3)*
C(34)	0.4647 (5)	0.364 (2)	0.2910 (6)	5.6 (3)*
C(35)	0.5230 (5)	0.385 (2)	0.2675 (7)	5.7 (3)*
C(36)	0.5319 (6)	0.335 (2)	0.2036 (7)	6.2 (3)*
C(37)	0.4877 (5)	0.266 (2)	0.1656 (6)	5.6 (3)*
C(38)	0.4330 (5)	0.246 (2)	0.1896 (6)	5.7 (3)*

* Atoms refined isotropically.

that the twist of the carbon framework is associated primarily with ring *A* and the bay C atoms bonded to it. Torsion angles associated with the bay C atoms [C(6)—C(16)—C(17)—C(7), 37(1)° and C(12)—C(13)—C(14)—C(1), 38(1)°] are quite large. The internal torsion angles in ring *A* are somewhat smaller and vary in magnitude from 16 (1) to 32 (1)° with the larger values associated with torsion about the *peri* bonds C(13)—C(14) and C(16)—C(17). In contrast to Cl₈DMP, perylene (1), both by itself (Camerman & Trotter, 1964) and in donor—acceptor complexes (Kozawa & Uchida, 1979), is essentially planar. Twisting about the *peri* bonds does not have a noticeable effect on the bond length: the C(13)—C(14) and C(16)—C(17) lengths are compar-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles for the benzene molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52419 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and angles (°)

Cl(1)—C(1)	1.712 (6)	C(4)—C(5)	1.398 (9)
Cl(2)—C(2)	1.711 (6)	C(4)—C(20)	1.386 (8)
Cl(5)—C(5)	1.716 (6)	C(4)—C(22)	1.490 (9)
Cl(6)—C(6)	1.754 (6)	C(5)—C(6)	1.427 (9)
Cl(7)—C(7)	1.743 (6)	C(6)—C(16)	1.361 (8)
Cl(8)—C(8)	1.744 (6)	C(7)—C(8)	1.396 (8)
Cl(11)—C(11)	1.724 (7)	C(7)—C(17)	1.370 (8)
Cl(12)—C(12)	1.733 (6)	C(8)—C(9)	1.367 (8)
O(1)—C(21)	1.210 (8)	C(9)—C(19)	1.431 (9)
O(2)—C(22)	1.198 (9)	C(9)—C(23)	1.478 (9)
O(3)—C(23)	1.208 (8)	C(10)—C(11)	1.358 (9)
O(4)—C(24)	1.211 (8)	C(10)—C(19)	1.423 (8)
N(1)—C(21)	1.389 (9)	C(10)—C(24)	1.464 (8)
N(1)—C(22)	1.398 (9)	C(11)—C(12)	1.405 (8)
N(1)—C(25)	1.499 (8)	C(12)—C(13)	1.389 (8)
N(2)—C(23)	1.405 (8)	C(13)—C(14)	1.460 (8)
N(2)—C(24)	1.379 (8)	C(13)—C(18)	1.443 (8)
N(2)—C(26)	1.466 (8)	C(14)—C(15)	1.427 (7)
C(1)—C(2)	1.423 (8)	C(15)—C(16)	1.398 (8)
C(1)—C(14)	1.402 (8)	C(15)—C(20)	1.386 (8)
C(2)—C(3)	1.38 (1)	C(16)—C(17)	1.498 (8)
C(3)—C(20)	1.452 (9)	C(17)—C(18)	1.408 (8)
C(3)—C(21)	1.493 (9)	C(18)—C(19)	1.418 (7)
C(21)—N(1)—C(22)	126.8 (5)	Cl(6)—C(6)—C(16)	122.3 (4)
C(21)—N(1)—C(25)	114.1 (5)	C(5)—C(6)—C(16)	122.0 (5)
C(22)—N(1)—C(25)	119.0 (6)	Cl(7)—C(7)—C(8)	118.1 (5)
C(23)—N(2)—C(24)	125.8 (5)	Cl(7)—C(7)—C(17)	120.2 (5)
C(23)—N(2)—C(26)	116.9 (5)	C(8)—C(7)—C(17)	121.5 (6)
C(24)—N(2)—C(26)	117.3 (6)	Cl(8)—C(8)—C(7)	117.3 (5)
Cl(1)—C(1)—C(2)	119.0 (5)	Cl(8)—C(8)—C(9)	121.1 (5)
Cl(1)—C(1)—C(14)	120.8 (4)	C(7)—C(8)—C(9)	121.3 (6)
C(2)—C(1)—C(14)	119.9 (5)	C(8)—C(9)—C(19)	119.1 (6)
Cl(2)—C(2)—C(1)	116.2 (6)	C(8)—C(9)—C(23)	122.3 (5)
Cl(2)—C(2)—C(3)	123.1 (5)	C(19)—C(9)—C(23)	118.5 (6)
C(1)—C(2)—C(3)	120.7 (5)	C(11)—C(10)—C(19)	118.5 (5)
C(2)—C(3)—C(20)	119.1 (5)	C(11)—C(10)—C(24)	122.4 (5)
C(2)—C(3)—C(21)	121.3 (6)	C(19)—C(10)—C(24)	119.0 (5)
C(20)—C(3)—C(21)	119.6 (6)	Cl(11)—C(11)—C(10)	123.0 (5)
C(5)—C(4)—C(20)	119.0 (5)	Cl(11)—C(11)—C(12)	115.9 (5)
C(5)—C(4)—C(22)	118.9 (6)	C(10)—C(11)—C(12)	120.9 (5)
C(20)—C(4)—C(22)	122.1 (6)	Cl(12)—C(12)—C(11)	118.2 (4)
Cl(5)—C(5)—C(4)	124.6 (5)	Cl(12)—C(12)—C(13)	119.5 (4)
Cl(5)—C(5)—C(6)	117.4 (5)	C(11)—C(12)—C(13)	122.1 (5)
C(4)—C(5)—C(6)	118.0 (5)	C(12)—C(13)—C(14)	126.8 (5)
Cl(6)—C(6)—C(5)	115.3 (4)	Cl(12)—C(13)—C(18)	116.2 (6)
Cl(14)—C(13)—C(18)	116.8 (5)	C(9)—C(19)—C(18)	117.6 (6)
C(1)—C(14)—C(13)	124.5 (5)	C(10)—C(19)—C(18)	120.4 (5)
C(1)—C(14)—C(15)	117.8 (5)	C(3)—C(20)—C(4)	119.6 (5)
C(13)—C(14)—C(15)	117.7 (5)	C(3)—C(20)—C(15)	119.3 (6)
C(14)—C(15)—C(16)	119.5 (6)	C(4)—C(20)—C(15)	121.0 (5)
C(14)—C(15)—C(20)	120.5 (5)	O(1)—C(21)—N(1)	120.3 (7)
C(16)—C(15)—C(20)	120.0 (5)	O(1)—C(21)—C(3)	123.5 (7)
C(6)—C(16)—C(15)	117.8 (5)	N(1)—C(21)—C(3)	116.1 (6)
C(6)—C(16)—C(17)	124.2 (6)	O(2)—C(22)—N(1)	119.8 (6)
C(15)—C(16)—C(17)	118.0 (5)	O(2)—C(22)—C(4)	124.9 (7)
C(7)—C(17)—C(16)	126.9 (5)	N(1)—C(22)—C(4)	115.3 (6)
C(7)—C(17)—C(18)	117.1 (5)	O(3)—C(23)—N(2)	118.7 (6)
C(16)—C(17)—C(18)	116.0 (5)	O(3)—C(23)—C(9)	124.3 (6)
C(13)—C(18)—C(17)	120.1 (5)	N(2)—C(23)—C(9)	117.0 (6)
C(13)—C(18)—C(19)	118.5 (5)	O(4)—C(24)—N(2)	119.7 (6)
C(17)—C(18)—C(19)	121.4 (6)	O(4)—C(24)—C(10)	122.5 (7)
C(9)—C(19)—C(10)	121.8 (5)	N(2)—C(24)—C(10)	117.8 (6)
Cl(1)—C(1)—C(14)—C(13)	22 (1)	C(18)—C(13)—C(14)—C(15)	31 (1)
Cl(6)—C(6)—C(16)—C(17)	14 (1)	C(13)—C(14)—C(15)—C(16)	-16 (1)
Cl(7)—C(7)—C(17)—C(16)	19 (1)	C(14)—C(15)—C(16)—C(17)	-16 (1)
Cl(12)—C(12)—C(13)—C(14)	13 (1)	C(15)—C(16)—C(17)—C(18)	32 (1)
Cl(12)—C(13)—C(14)—C(11)	38 (1)	C(16)—C(17)—C(18)—C(13)	-16 (1)
C(6)—C(16)—C(17)—C(7)	37 (1)	C(14)—C(13)—C(18)—C(17)	-15 (1)

found to have a similarly deformed structure (Graser & Haedicke, 1985). The Cl(6)⋯Cl(7) and Cl(1)⋯Cl(12) distances [3.109 (3) and 3.136 (3) Å, respectively] are comparable to the non-bonding Cl⋯Cl bay interactions in the crowded phenanthrene derivatives (2) (3.10 Å) and (3) (3.10 Å) (Cosmo, Hambley & Sternhell, 1987). Other examples of highly twisted hydrocarbons are known. In 9,18-diphenyltetrabenz[*a,c,h,i*]anthracene (4), the anthracene fragment is twisted 65.7° end-to-end. In this instance, twisting results from severe C⋯H non-bonded interactions (Pascal, McMillan & Van Engen, 1986). Short Cl⋯Cl contacts from *peri*-related atoms can also distort a hydrocarbon framework. In perchlorocoronene, the unique *peri* Cl⋯Cl contacts are 3.021 (2) and 3.045 (1) Å. The molecule shows substantial deviations from planarity and exhibits very nearly D_{3d} symmetry (Baird, Gall, MacNicol, Mallinson & Michie, 1988).

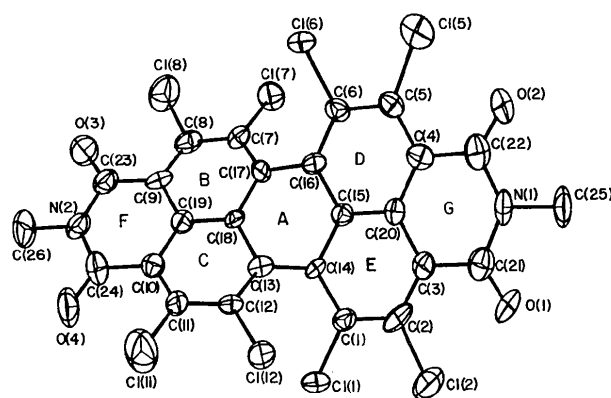


Fig. 1. View of the Cl₈DMP molecule showing the atom-numbering scheme. C atoms of the benzene molecules (not shown) are numbered C(27) to C(32) and C(33) to C(38).

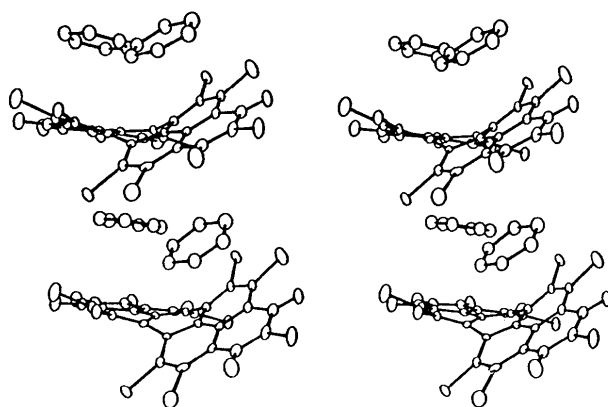
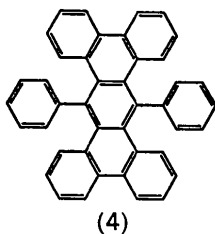
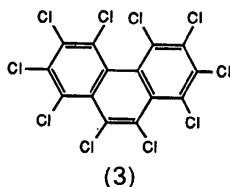
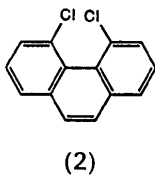
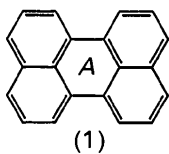


Fig. 2. Partial view of the structure showing stacking along the *b* (vertical) direction and twisting of the central ring in Cl₈DMP.

able to those in perylene by itself and in several complexes [1.473 (5) Å (Hanson, 1963); 1.463 (5), 1.479 (5) Å (Cameran & Trotter, 1964); 1.47 (1) Å (Kozawa & Uchida, 1979); 1.482 (6) Å (Kozawa & Uchida, 1983)]. The twisting in Cl₈DMP arises from steric crowding associated with bay (6,7) and bay (1,12) interactions. The crystal structure of a 1,6,7,12-tetrachloroperylene derivative has been



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Methyl *trans*-2-(Diphenylmethyl)-5-(hydroxymethyl)-3-isoxazolidinylacetate and *cis*-5-(Ethoxymethyl)-2-phenyl-3-isoxazolidinyl Phenyl Ketone

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Abstract. C₁₉H₂₁NO₄ (1): $M_r = 327.38$, monoclinic, $P2_1/n$, $a = 10.103$ (3), $b = 20.253$ (4), $c = 9.273$ (2) Å, $\beta = 115.49$ (2)°, $V = 1713$ (1) Å³, $Z = 4$, $D_m = 1.25$ (2), $D_x = 1.27$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.52$ cm⁻¹, $F(000) = 696.0$. Final conventional $R = 0.046$ for 2742 unique observed reflections. C₁₉H₂₁NO₃ (2): $M_r = 311.37$, orthorhombic, $Pbca$, $a = 18.213$ (3), $b = 20.451$ (4), $c = 8.904$ (2) Å, $V = 3317$ (3) Å³, $Z = 8$, $D_m = 1.24$ (2), $D_x = 1.25$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.48$ cm⁻¹, $F(000) = 1328.0$. Final conventional $R = 0.066$ for 1836 unique observed reflections. The stereochemistry of both compounds was established unequivocally. The conformation of the isoxazolidine ring of (1) has approximate C_2 symmetry through C(5), while that

of (2) has C_s symmetry, N(2) being the out-of-plane atom. Two substituents at N(2) and C(3) of both compounds have a *trans*-diaxial orientation in the crystal structure.

Introduction. The investigation of regio- and stereo-selectivities in the 1,3-dipolar cycloaddition of nitrones is one of the most stimulating problems from both theoretical and synthetic points of view (Padwa, 1984). In order to clarify the selectivities, it is essential to elucidate the stereochemistry of the isoxazolidine ring. However, it is sometimes difficult to assign the stereochemistry by ordinary ¹H NMR techniques because the isoxazolidine ring may exist in many different conformers.