

31 220 cm<sup>-1</sup>, attributed to metal-to-benzene charge transfer with some metal-to-CO charge transfer (Geoffroy & Wrighton, 1979). The net charge transfer in that molecule should be along the direction from the centroid of the (CO)<sub>3</sub> group through the chromium atom to the centroid of the six-membered ring, and there should be a similarly directed transfer in the styrene analog. It seems reasonable to assume that the tricarbonyl(styrene)chromium molecule is a 'one-dimensional' charge-transfer system with a single significant second-order molecular hyperpolarizability,  $\beta_{uuu}$ , in the direction indicated.

For a crystal of class 222 of such a molecule, symmetry and the Kleinman (1962) relations allow only a single macroscopic second-order hypopolarizability coefficient,  $d_{xyz}$ . That coefficient has been shown by Zyss & Oudar (1982) to be proportional to the unique molecular hyperpolarizability coefficient and to the product  $\sin\varphi\cos\varphi\cos\theta\sin^2\theta$ , where  $\varphi$  and  $\theta$  are spherical polar coordinates defining the orientation of the transfer vector with respect to Cartesian base vectors parallel to the unit-cell axes. The trigonometric function of  $\varphi$  and  $\theta$  is equivalent to the product of the three direction cosines of the vector. For the disordered molecule of tricarbonyl(styrene)chromium in the crystal we take the transfer direction to be along the best least-squares line through the 12 atoms of the two fractional C rings and the seven atoms of the Cr(CO)<sub>3</sub> group. The direction cosines  $\cos\theta_x$ ,  $\cos\theta_y$ , and  $\cos\theta_z$  are -0.4121 (16), -0.2158 (18), and 0.8852 (7); and their product is 0.0787 (1), to be compared with the extreme or optimal values  $\pm 1/3\sqrt{3} = \pm 0.1925$  of the cosine product, which correspond to values of  $\arccos(\pm 1/\sqrt{3})$  for each of  $\theta_x$ ,  $\theta_y$ , and  $\theta_z$  (either 54.74 or 125.26° for each). The orientation of the tricarbonyl(styrene)chromium molecule clearly is not optimal for second-harmonic generation.

A more favorable orientation could have increased the magnitude of  $d_{xyz}$  by a factor as large as

$0.1925/0.0787 = 2.44$  and the efficiency of harmonic generation by as much as that factor squared,  $\sim 6$ . It is therefore possible that so-called 'molecular and crystal engineering' can be used to produce a similar molecule with as good or better molecular polarizability properties in an acentric crystal in which the molecule has an orientation more favorable for efficient harmonic generation. The preference, of course, is for a crystal of one of the classes 2,  $m$  and  $mm2$ , for which with the same molecular polarizability there can in principle be one or more macroscopic polarizability coefficients with maximum magnitude twice that of the single coefficient allowed for class 222 (Zyss & Oudar, 1982) and therefore an increase in s.h.g. efficiency over that of the crystal used in this study by a factor of  $\sim 24$ .

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### Structure of 4-Methoxy-1-(*N*-phenyl)iminonaphthalene

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**Abstract.** C<sub>18</sub>H<sub>15</sub>NO,  $M_r = 261.32$ , monoclinic,  $P2_1/c$ ,  $a = 10.280$  (2),  $b = 16.731$  (3),  $c = 8.027$  (1) Å,  $\beta = 90.33$  (2)°,  $V = 1380.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.257$  g cm<sup>-3</sup>,

Mo  $K\alpha$  radiation (graphite-monochromated),  $\lambda = 0.70926$  Å,  $\mu = 0.84$  cm<sup>-1</sup>,  $F(000) = 552$ ,  $T = 293$  K, 2426 unique reflections, 915 with  $I > 2\sigma(I)$ , final

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$R = 0.037$ . Evidence of significant  $\pi$ -electron delocalization is shown by the short bond lengths for C(1)—CH(N) = 1.458 (5), N—C(Ph) = 1.410 (4) and C(4)—O = 1.360 (4) Å. The aniline ring is twisted out of the C—N=C—C plane by 46.2° and the naphthyl rings are twisted similarly by 18.2°.

**Introduction.** X-ray structure determinations of *N*-benzylideneaniline and some of its derivatives (Bürgi & Dunitz, 1970; Bernstein, 1972) have shown that the aniline ring is twisted out of the C—N=C—C plane by amounts varying from 38 to 55°, and that the benzylidene ring also lies out of the plane with a smaller twist of 6–14°. Molecular conformation calculations (Bürgi & Dunitz, 1971) have shown that the twist angle corresponds to the potential-energy minimum obtained by combining the  $\pi$ -electron energy of a completely delocalized system with non-bonded intramolecular interactions. The present paper reports the structure of a related ylidene-aniline which exhibits similar twist angles.

**Experimental.** The title compound was prepared by refluxing 4-methoxy-1-naphthaldehyde with aniline in methanol for one day. Crystal dimensions 0.3 × 0.3 × 0.2 mm, Enraf-Nonius CAD-4 diffractometer, lattice parameters from 25 reflections with  $\theta = 10$ –14°. Intensities for  $\theta < 25^\circ$ ,  $hkl$ : -1 to 12, -1 to 19, -9 to 9,  $\omega$ -2 $\theta$  scan,  $\omega$ -scan width (1.0 + 0.35tan $\theta$ )° at 0.7–4.0° min<sup>-1</sup>, extended 25% on each side for background measurement; three standard reflections showed negligible variation in intensity, intensities reduced to a standard scale (Cameron & Cordes, 1979), Lp corrections applied, no corrections for absorption. 3187 reflections measured, 2426 unique ( $R_{\text{int}} = 0.046$ ) and 915 considered observed with  $I > 2\sigma(I)$ . The structure was solved by direct methods which revealed positions for all of the non-H atoms. H-atom positions were found from a difference-Fourier synthesis and their positions were not refined. Anisotropic refinement (on  $F$ ) of the non-hydrogen atoms and refinement of individual isotropic temperature factors on the H atoms employed a two-block matrix least-squares method, which minimized  $\sum w(|F_o| - |F_c|)^2$  where  $w = 0.125/[\sigma^2(F_o) + 0.002|F_o|^2]$ . The refinement converged at  $R = 0.037$ ,  $wR = 0.038$  for 915 observed reflections, 204 parameters,  $(\Delta/\sigma)_{\text{max}} = 0.6$ , max. and min. heights in final difference Fourier map = 0.12 and -0.17 e Å<sup>-3</sup>. An empirical correction was applied for extinction. Scattering factors for neutral atoms were obtained from *International Tables for X-ray Crystallography* (1974) and were corrected for the real part of anomalous dispersion. Computer programs used were *SHELX76* (Sheldrick, 1976) and *CHEMGRAF* (Davies, 1983).

Table 1. Fractional positional and equivalent isotropic thermal parameters (Å<sup>2</sup>) with e.s.d.'s in parentheses

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
N	0.7299 (2)	0.1368 (1)	0.8338 (3)	0.0636
O	0.1820 (2)	-0.0058 (1)	0.5540 (2)	0.0717
C(1)	0.5460 (3)	0.0543 (2)	0.7483 (3)	0.0509
C(2)	0.4891 (3)	-0.0176 (2)	0.7844 (3)	0.0570
C(3)	0.3668 (3)	-0.0401 (2)	0.7240 (3)	0.0580
C(4)	0.3012 (3)	0.0100 (2)	0.6208 (3)	0.0568
C(5)	0.3547 (3)	0.0848 (2)	0.5745 (3)	0.0499
C(6)	0.2897 (3)	0.1359 (2)	0.4614 (3)	0.0614
C(7)	0.3437 (3)	0.2066 (2)	0.4133 (4)	0.0662
C(8)	0.4631 (3)	0.2298 (2)	0.4755 (3)	0.0632
C(9)	0.5295 (3)	0.1821 (2)	0.5863 (3)	0.0561
C(10)	0.4776 (3)	0.1081 (2)	0.6389 (3)	0.0501
C(11)	0.8555 (3)	0.1408 (2)	0.9050 (3)	0.0557
C(12)	0.8834 (3)	0.2025 (2)	1.0167 (4)	0.0670
C(13)	1.0049 (3)	0.2100 (2)	1.0833 (4)	0.0738
C(14)	1.1021 (3)	0.1587 (2)	1.0384 (4)	0.0732
C(15)	1.0768 (3)	0.0983 (2)	0.9267 (4)	0.0732
C(16)	0.9539 (3)	0.0898 (2)	0.8606 (3)	0.0651
C(17)	0.6730 (3)	0.0700 (2)	0.8233 (3)	0.0565
C(18)	0.1206 (3)	-0.0786 (2)	0.5994 (4)	0.0845

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

C(1)—C(2)	1.368 (5)	C(9)—C(10)	1.414 (5)
C(1)—C(10)	1.439 (4)	C(1)—C(17)	1.458 (5)
C(2)—C(3)	1.397 (5)	C(17)—N	1.265 (5)
C(3)—C(4)	1.356 (5)	N—C(11)	1.410 (4)
C(4)—C(5)	1.416 (5)	C(11)—C(12)	1.397 (5)
C(4)—O	1.360 (4)	C(11)—C(16)	1.372 (5)
C(5)—C(6)	1.413 (5)	C(12)—C(13)	1.362 (5)
C(5)—C(10)	1.417 (5)	C(13)—C(14)	1.367 (5)
C(6)—C(7)	1.363 (5)	C(14)—C(15)	1.374 (5)
C(7)—C(8)	1.378 (5)	C(15)—C(16)	1.374 (5)
C(8)—C(9)	1.374 (5)	O—C(18)	1.421 (5)
C(2)—C(1)—C(10)	118.1 (3)	C(1)—C(10)—C(5)	118.8 (3)
C(2)—C(1)—C(17)	117.0 (3)	C(1)—C(10)—C(9)	123.1 (3)
C(10)—C(1)—C(17)	124.9 (3)	C(5)—C(10)—C(9)	118.0 (3)
C(1)—C(2)—C(3)	123.3 (3)	C(12)—C(11)—C(16)	118.5 (3)
C(2)—C(3)—C(4)	119.2 (3)	C(12)—C(11)—N	118.6 (3)
C(3)—C(4)—C(5)	120.9 (3)	C(16)—C(11)—N	122.8 (3)
C(3)—C(4)—O	124.3 (3)	C(11)—C(12)—C(13)	120.3 (3)
C(5)—C(4)—O	114.8 (3)	C(12)—C(13)—C(14)	120.6 (3)
C(4)—C(5)—C(6)	121.3 (3)	C(13)—C(14)—C(15)	119.8 (4)
C(4)—C(5)—C(10)	119.6 (3)	C(14)—C(15)—C(16)	119.9 (4)
C(6)—C(5)—C(10)	119.0 (3)	C(11)—C(16)—C(15)	120.9 (3)
C(5)—C(6)—C(7)	121.0 (3)	C(1)—C(17)—N	126.8 (3)
C(6)—C(7)—C(8)	120.4 (3)	C(11)—N—C(17)	119.4 (3)
C(7)—C(8)—C(9)	120.6 (3)	C(4)—O—C(18)	117.8 (3)
C(8)—C(9)—C(10)	121.0 (3)		

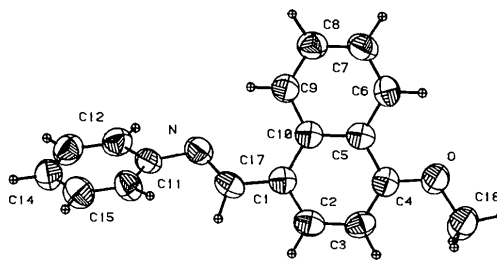


Fig. 1. View of the title compound showing the atom numbering (Davies, 1983).

**Discussion.** Atomic positional parameters are listed in Table 1, bond lengths and angles in Table 2, and a view of the molecule is shown in Fig. 1.\* The mean C—C bond lengths of 1.37 (1) Å in the aniline ring and 1.39 (3) Å in the naphthalene rings are normal. The C(1)—C(17)=N bond angle is larger than expected. The significance of this is discussed below.

The C—C=N—C link between the rings should be involved in a delocalized  $\pi$ -electron system and the bond lengths in this bridge can be used to provide some measure of the contribution of resonance forms to the electronic structure. Evidence of significant conjugation between the rings is shown by the short single-bond lengths for C(1)—C(17) [1.458 (5) Å] and N—C(11) [1.410 (4) Å] and a long C(17)=N bond [1.265 (5) Å]. X-ray structure determinations of *N*-benzylideneaniline and some of its derivatives (Bürgi & Dunitz, 1970) have shown that the C—N single-bond distance is further shortened and the C=N bond distance is lengthened with an increase in the electronegativity of *para* substituents on the aniline ring as a result of greater contributions of quinoid structures to the resonance forms. An analogous effect was noted (Bernstein, 1972) when 2,4-dichloro substituents were placed on the benzyl ring of *N*-benzylideneaniline. Similarly, the title compound contains a 4-methoxy substituent on the naphthyl group which contributes to the shortening of the C(1)—C(17) and N—C(11) bonds and the lengthening of the C(17)=N bond. The C(4)—O bond length [1.360 (4) Å] is also quite short, which confirms the contribution of the methoxy group to the quinoid resonance structure. Table 3 compares bond lengths within the imine link of the title compound with those of several benzylideneaniline derivatives and shows that the methoxy group contributes approximately the same resonance energy as *p*-nitro or 2,4-dichloro substituents, although additional stabilization of the quinoid resonance form may be attributed to the replacement of the benzyl group by a naphthyl group.

The most significant feature of the molecule is the twist of the aniline ring out of the C(1)—C(17)=N—C(11) plane by 46.2° and the smaller twist of the naphthalene rings out of this plane by 18.2°. This observation is consistent with the twists observed for benzylideneaniline and its derivatives (Bürgi & Dunitz, 1970; Bernstein, 1972) which fall into the range of 38–55° for the aniline ring and 6–14° for the benzylidene ring. Molecular conformation calculations (Bürgi & Dunitz, 1971) have shown that the out-of-plane twists correspond to a potential-energy

\* Lists of anisotropic thermal parameters, H-atom positions, bond lengths and angles involving H, torsion angles, least-squares-planes calculations and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51760 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Comparison of bond lengths (Å) within the imine link

Atom numbering corresponds to Fig. 1.

	C(11)—N	N=C(17)	C(17)—C(1)
4-Methoxy-1-( <i>N</i> -phenyl)-iminonaphthalene	1.410	1.265	1.458
Benzylideneaniline*	1.460	1.237	1.496
Benzylideneaniline- <i>p</i> -carboxylic acid*	1.431	1.281	1.461
<i>N</i> -(4-Methylbenzylidene)- <i>p</i> -nitroaniline*	1.400	1.260	1.474
<i>N</i> -(2,4-Dichlorobenzylidene)-aniline†	1.407	1.268	1.482

\* Bürgi & Dunitz (1970).

† Bernstein (1972).

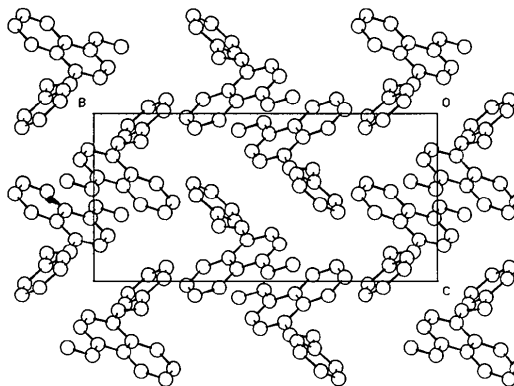


Fig. 2. Projection of the unit-cell packing down the *a* axis.

minimum. These calculations take into account both  $\pi$ -electron energies, which, as expected for a resonance structure, are at a minimum for a completely planar system, and non-bonded intramolecular interactions which have a maximum potential energy when the rings lie in the imine plane. The twist of the plane of the naphthyl rings from the imine plane is greater than any observed previously for the benzylidene rings, and is probably caused by increased non-bonded interactions between the N atom and C(9) and H(9) compared with the benzylidene compounds which only have a H atom in place of C(9). The large C(1)—C(17)=N bond angle of 126.8 (3)° may also be the result of these non-bonded interactions. The sense of rotation of the aniline ring is opposite to that of the naphthyl group. This is consistent with most previous cases although there is one exception (Bernstein, 1972). The relative sense of the twists for these molecules is probably determined by the most favorable packing arrangement. The packing is shown in Fig. 2.

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### Platelet Activating Factor Antagonist Design. 3. X-ray Crystal Structure and Intermolecular Crystal Lattice Interactions of Methyl *trans*-4-Acetoxyethyl-4,5-dihydro-2,5-bis(3,4-methylenedioxyphenyl)-3-furancarboxylate

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**Abstract.** C<sub>23</sub>H<sub>20</sub>O<sub>9</sub>, *M<sub>r</sub>* = 440.41, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.433 (1), *b* = 7.808 (2), *c* = 23.313 (3) Å, β = 99.67 (1)°, *V* = 2052 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.43 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 0.69 cm<sup>-1</sup>, *F*(000) = 920, *T* = 293 K, final *R* = 0.048 for 1645 observed [*F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*)] reflections. The observed structure reveals a *trans* relationship for the 4-acetoxyethyl and 5-aryl substituents. The 4,5-dihydrofuran ring system adopts an envelope conformation. There is no crystallographically imposed symmetry. Several intermolecular van der Waals interactions occur in the cell lattice of this compound.

**Introduction.** Platelet-activating-factor (PAF) is an important mediator of mammalian cell function and it is thought to play a significant role in several alterations of the pulmonary, intravascular, and cardiovascular systems (Venuti, 1985; McManus, 1986; Etienne, Hecquet & Braquet, 1988; Smith, Rubin & Patterson, 1988). The specific binding of PAF to cellular membrane receptor sites is the first step in its biological functions (McManus, 1986; Hwang, Lam, Biftu, Beattie & Shen, 1985). Potent and selective PAF antagonists provide leads to the molecular characteristics of the PAF receptor site in addition to serving

as therapeutically effective agents (Braquet & Godfroid, 1986; Godfroid & Braquet, 1986; Corey, Chen & Parry, 1988). We recently reported some early investigations aimed at the design of such antagonists (Peterson, Smillie & Rogers, 1989; Peterson, Do & Rogers, 1989), which were modeled upon naturally occurring furanoid lignans (Braquet & Godfroid, 1986; Biftu & Stevenson, 1987) and Merck Sharp & Dohme's potent PAF antagonists L-652,732 and L-659,989 (Hwang *et al.*, 1985; Biftu, Gamble, Doebber, Hwang, Shen, Snyder, Springer & Stevenson, 1986; Wu, Biftu & Doebber, 1986; Ponpipom, Hwang, Doebber, Acton, Alberts, Biftu, Brooker, Bugianesi, Chabala, Gamble, Graham, Lam & Wu, 1988). In our approach, X-ray crystallography is projected to provide not only detail about the three-dimensional topography of a compound and its congeneric series, but also information about the molecular nature of the biological receptor site through an understanding of the intermolecular interactions that stabilize the crystal lattice (Coddling & Muir, 1985; Coddling, 1988). Herein we describe the X-ray crystal structure and an analysis of the closest contacts between neighboring molecules in the crystal lattice for the title compound, prepared en route to hinokin, a phytolignan member of the PAF-antagonistic family of prestegane natural products (Braquet & Godfroid, 1986).

**Experimental.** The title dihydrofuran was prepared in 43% isolated yield by manganese(III) acetate oxidation

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