benzoctamine. Cette observation, en concordance avec les résultats de la RMN, permet d'envisager une similitude des conformations d'énergie minimum dans l'état solide cristallin et dans l'état liquide dissous.

En raison des analogies structurales existant entre d'une part le dibenzobicyclooctadiène et ses dérivés et d'autre part les composés tricycliques, nous pouvons comparer les valeurs de l'angle de pliage α mesurées pour les deux composés étudiés dans ce travail (α = 118 et α = 121° respectivement) avec les valeurs moyennes calculées pour une série de dérivés tricycliques non pontés des types 6–6–6 (α = 143°) et 6–7–6 (α = 120°) (Reboul, 1983).

Ces valeurs permettent de constater que la famille du dibenzobicyclooctadiène, bien qu'assimilable par son cycle central aux dérivés du type 6–6–6, se rapprocherait plutôt par la valeur de l'angle de pliage α des dérivés du type 6–7–6.

Rappelons par ailleurs que la benzoctamine appartient à la classe pharmacologique des tranquillisants (Baltzer & Bein, 1973) qui comprend plusieurs séries chimiques très différentes, dont la plus représentative est certainement celle des benzodiazépines.

Des études ont été menées sur ces derniers composés (Camerman & Camerman, 1971, 1972; Sternbach, Sancilio & Blount, 1974) en vue d'établir des corrélations entre leur stéréochimie et leur activité biologique. Aux conclusions de ces auteurs nous pouvons rattacher nos observations, en effet toutes ces substances non seulement se caractérisent par la présence d'atomes d'azote ou d'oxygène situés à un ou deux chaînons d'un des cycles aromatiques, mais encore, il apparaît que l'angle de pliage des benzodiazépines, voisin de 120°, est très proche de celui relevé chez la benzoctamine et son dérivé perméthylé.

La benzoctamine et son dérivé de perméthylation nous ont été aimablement fournis par les laboratoires CIBA-GEIGY.

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Structure of 3,7-Bis(N,N-diethylamino)-10-benzoylphenoxazine (BLASB), C₂₇H₃₁N₃O₂

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Abstract. $M_r = 429.56$, $P\bar{1}$, $a = 8.667$ (1), $b = 8.742$ (1), $c = 16.382$ (3) Å, $\alpha = 87.34$ (1), $\beta = 84.31$ (1), $\gamma = 69.32$ (1)°, $V = 1155.4$ (5) Å³, $Z = 2$, $D_x = 1.239$ g cm⁻³, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 5.42$ cm⁻¹, $F(000) = 460.0$, room temperature, final $R = 0.0481$ for 3183 unique reflections. BLASB is a commercially available leucodye. The two N,N-diethyls are chemically identical but crystallographically distinct, with one ethyl group disordered at two cl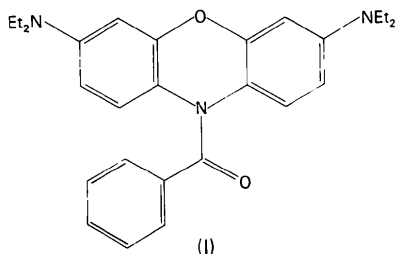early distinguishable positions. Delocalization of electrons occurs over the benzene ring, carbonyl group and the nitrogen lone pair. The molecule has, as expected, a propeller-like shape.

Introduction. Leucodyes are technologically very interesting materials because, whilst normally colourless, upon reaction with a substrate, e.g. a solid surface, they yield intensely coloured species. A similar property is exhibited by a variety of aromatic compounds, such as benzidine (Tennakoon, Thomas, Tricker & Williams,

Table 1. *Data collection and refinement details*

Lattice constants determination

number of reflections	25
θ, min., max. (°)	20,30
Total data collected	4678
Total data unique	3971
θ range min., max. (°)	3,70
h min., max.	0,10
k min., max.	−10,10
l min., max.	−19,19
R_{int}	0·0326
Unobserved reflections	992
Significance test	$F_o > 3\sigma(F_o)$
Parameters refined	446
R	0·0481
R_w	0·0451
Weighting scheme	$[\sigma^2 F + 0\cdot0007 F^2]^{-1}$
Final cycle	
max. Δ/σ	0·145
max. ΔF peak (e Å^{-3})	0·20

1974), triphenylmethanol (Fripiat, Helsen & Vielvoye, 1964) and crystal violet lactone (CVL, Fahn & Fenderl, 1983). As part of an investigation into the interaction of organic molecules with surfaces (Theocharis & Jones, 1984; Theocharis, 1982), we report here the crystal structure of the title compound BLASB (I, trivial name: benzoyl leocoaevonal), a commercially available leucodye. The crystal and molecular structure may shed some light into the colouring mechanism or mode of interaction of BLASB with the substrate.

(I)

Experimental. Table 1 contains data collection and refinement details. Single crystals obtained by slow evaporation of dilute chloroform–methanol solution. Crystal 0·35 × 0·20 × 0·10 mm, fragment of prism. Intensity data and lattice parameters obtained on Enraf–Nonius CAD-4 four-circle diffractometer, ω–2θ scan mode in manner previously described (Hursthouse, Jones, Malik & Wilkinson, 1979). No absorption correction. 2 standard reflections (334, 325), intensity variation <1·5%. Structure solved by direct methods and refined isotropically using full-matrix least squares. Anisotropic refinement based on F by block cascaded full least-squares techniques. Hydrogen atoms located from difference Fourier maps and refined. One of the ethyl groups was found to be disordered and was resolved at two different positions designated A and B. Occupancy factor of A set at x and of B at $(1-x)$; x allowed to refine, converged to 0·531 (3). Hydrogen atoms belonging to each carbon of this ethyl group

assigned a common and the rest individual isotropic thermal parameters. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were performed on an IBM-3081 computer with *SHELX*76 (Sheldrick, 1976), *PLUTO*78 (Motherwell & Clegg, 1978), *ORTEP* (Johnson, 1965), *GEOM*78 (Cartwright, 1978) and private programs.

Discussion. Fig. 1 contains the atomic numbering scheme, whilst final atomic parameters are presented in Table 2, and bond lengths and angles in Table 3.*

The two *N,N*-diethyl groups are chemically equivalent but, as can be seen from Fig. 2, are crystallographically distinct. One of the two *N,N*-diethyls [N(1), C(20), C(21), C(22), C(23)] takes part in a larger number of short non-bonded contacts than the second group. The presence of disorder in one of the ethyls may therefore be due to steric effects.

* Lists of structure factors, anisotropic thermal parameters and non-bonded contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39471 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
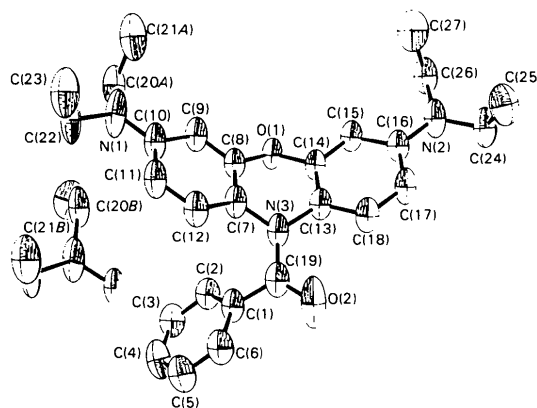

Fig. 1. *ORTEP* (Johnson, 1965) plot for BLASB, showing the atom numbering scheme. The inset shows position B for the disordered ethyl group.
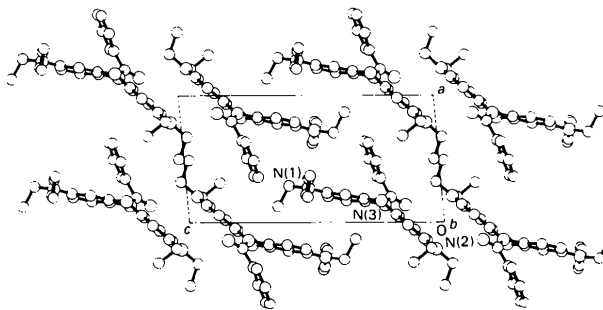

Fig. 2. Crystal structure of BLASB viewed along [010].

Table 2. *Atom coordinates* (×10⁴) *for BLASB*

$U_{eq} = 0.33$ trace $(\tilde{U})$.

	x	y	z	$U_{eq}/U_{iso}(\text{Å}^2)$
C(1)	3518 (3)	4886 (2)	2351 (1)	0.045
C(2)	4871 (3)	3478 (3)	2468 (1)	0.052
C(3)	6298 (3)	3593 (3)	2710 (2)	0.062
C(4)	6392 (3)	5092 (3)	2857 (2)	0.066
C(5)	5068 (3)	6493 (3)	2741 (2)	0.063
C(6)	3644 (3)	6395 (3)	2477 (1)	0.055
C(7)	1694 (3)	2815 (2)	3033 (1)	0.043
C(8)	1882 (2)	1183 (2)	3072 (1)	0.041
C(9)	2213 (3)	264 (2)	3782 (1)	0.048
C(10)	2364 (3)	974 (3)	4504 (1)	0.052
C(11)	2092 (3)	2652 (3)	4474 (1)	0.054
C(12)	1759 (3)	3549 (3)	3752 (1)	0.051
C(13)	460 (3)	3052 (2)	1759 (1)	0.042
C(14)	635 (2)	1417 (2)	1851 (1)	0.040
C(15)	−206 (3)	691 (2)	1431 (1)	0.043
C(16)	−1280 (3)	1594 (2)	851 (1)	0.045
C(17)	−1431 (3)	3244 (3)	741 (1)	0.050
C(18)	−602 (3)	3955 (2)	1186 (1)	0.048
C(19)	2017 (3)	4849 (2)	1996 (1)	0.050
C(20A)	3476 (6)	−1779 (6)	5159 (3)	0.063
C(20B)	2210 (7)	−1463 (6)	5317 (3)	0.054
C(21A)	2053 (7)	−2403 (7)	5263 (3)	0.079
C(21B)	3703 (9)	−2973 (7)	5102 (4)	0.079
C(22)	2920 (4)	746 (3)	5965 (2)	0.070
C(23)	1312 (4)	1583 (4)	6466 (2)	0.087
C(24)	−3239 (3)	1824 (3)	−186 (1)	0.060
C(25)	−4946 (3)	2790 (3)	188 (2)	0.078
C(26)	−2033 (3)	−787 (3)	587 (1)	0.056
C(27)	−3154 (4)	−952 (3)	1335 (2)	0.072
O(1)	1730 (2)	402 (2)	2385 (1)	0.046
O(2)	1395 (2)	5834 (2)	1461 (1)	0.078
N(1)	2738 (3)	43 (3)	5211 (1)	0.074
N(2)	−2102 (2)	879 (2)	406 (1)	0.053
N(3)	1398 (2)	3641 (2)	2255 (1)	0.044
H(11A)	4345 (39)	−2440 (37)	5613 (20)	0.047 (6)
H(12A)	4233 (39)	−2527 (37)	4526 (20)	0.047 (6)
H(21A)	1257 (50)	−1594 (46)	4945 (28)	0.097 (6)
H(22A)	1485 (51)	−2074 (48)	5843 (34)	0.097 (6)
H(23A)	2619 (51)	−3802 (49)	5120 (30)	0.097 (6)
H(11B)	8292 (56)	1447 (53)	4116 (37)	0.093 (7)
H(12B)	3530 (56)	−3706 (54)	5181 (34)	0.093 (7)
H(21B)	4671 (70)	−2529 (68)	4903 (49)	0.234 (8)
H(22B)	958 (71)	8731 (67)	5029 (49)	0.234 (8)
H(23B)	1498 (71)	−2644 (69)	4638 (50)	0.234 (8)
H(2)	4797 (22)	2434 (21)	2324 (11)	0.045 (5)
H(3)	7263 (31)	2604 (29)	2724 (15)	0.099 (6)
H(4)	7382 (28)	5189 (26)	3020 (14)	0.086 (6)
H(5)	5073 (27)	7636 (25)	2839 (14)	0.080 (6)
H(6)	2693 (28)	7353 (26)	2445 (14)	0.081 (6)
H(9)	2275 (23)	−807 (21)	3760 (11)	0.048 (5)
H(11)	2124 (26)	3260 (24)	4989 (13)	0.069 (5)
H(12)	1566 (24)	4772 (23)	3766 (12)	0.060 (5)
H(15)	−36 (21)	−445 (20)	1534 (10)	0.039 (4)
H(17)	7802 (25)	3909 (23)	398 (12)	0.061 (5)
H(18)	9269 (25)	5102 (24)	1091 (12)	0.063 (5)
H(221)	3554 (26)	1489 (25)	5856 (13)	0.074 (5)
H(222)	3825 (29)	−288 (28)	6276 (15)	0.091 (6)
H(231)	509 (35)	2530 (33)	6131 (18)	0.127 (7)
H(232)	1547 (32)	2168 (30)	6981 (17)	0.110 (6)
H(233)	712 (35)	804 (33)	6687 (18)	0.130 (7)
H(241)	−2762 (29)	2553 (28)	−548 (15)	0.090 (6)
H(242)	−3327 (28)	964 (26)	−589 (14)	0.083 (6)
H(251)	−4925 (30)	3655 (28)	593 (16)	0.093 (6)
H(252)	−5566 (35)	2041 (34)	518 (18)	0.131 (7)
H(253)	−5677 (34)	3404 (32)	−240 (17)	0.119 (7)
H(261)	−901 (24)	−1492 (22)	699 (12)	0.058 (5)
H(262)	−2338 (24)	−1241 (23)	81 (12)	0.059 (5)
H(271)	−2922 (32)	−2136 (30)	1430 (16)	0.107 (6)
H(272)	−4329 (30)	−407 (27)	1289 (15)	0.093 (6)
H(273)	−2940 (29)	−428 (27)	1810 (14)	0.085 (6)

Table 3. *Bond lengths* (Å) *and angles* (°) *for BLASB*

Bond	Length	Bond	Length
C(1)–C(2)	1.389 (4)	C(1)–C(6)	1.388 (4)
C(1)–C(19)	1.488 (5)	C(2)–C(3)	1.374 (5)
C(3)–C(4)	1.375 (5)	C(4)–C(5)	1.372 (4)
C(5)–C(6)	1.379 (5)	C(7)–C(8)	1.377 (4)
C(7)–C(12)	1.381 (4)	C(7)–N(3)	1.436 (3)
C(8)–C(9)	1.376 (4)	C(8)–O(1)	1.384 (4)
C(9)–C(10)	1.399 (4)	C(10)–C(11)	1.401 (4)
C(10)–N(1)	1.381 (4)	C(11)–C(12)	1.386 (4)
C(13)–C(14)	1.386 (4)	C(13)–C(18)	1.393 (4)
C(13)–N(3)	1.433 (4)	C(14)–C(15)	1.370 (4)
C(14)–O(1)	1.397 (3)	C(15)–C(16)	1.407 (4)
C(16)–C(17)	1.406 (4)	C(16)–N(2)	1.375 (4)
C(17)–C(18)	1.377 (5)	C(19)–O(2)	1.222 (4)
C(19)–N(3)	1.377 (4)	C(20A)–C(21A)	1.507 (11)
C(20A)–N(1)	1.496 (6)	C(20B)–C(21B)	1.512 (9)
C(20B)–N(1)	1.536 (9)	C(22)–C(23)	1.503 (6)
C(22)–N(1)	1.451 (5)	C(24)–C(25)	1.504 (5)
C(24)–N(2)	1.461 (4)	C(26)–C(27)	1.520 (6)
C(26)–N(2)	1.455 (4)		

Angle	(°)	Angle	(°)
C(2)–C(1)–C(6)	118.9 (3)	C(2)–C(1)–C(19)	122.3 (3)
C(6)–C(1)–C(19)	118.4 (3)	C(1)–C(2)–C(3)	120.0 (3)
C(2)–C(3)–C(4)	120.6 (3)	C(3)–C(4)–C(5)	120.0 (4)
C(4)–C(5)–C(6)	119.9 (4)	C(1)–C(6)–C(5)	120.6 (3)
C(8)–C(7)–C(12)	117.5 (3)	C(8)–C(7)–N(3)	117.7 (3)
C(12)–C(7)–N(3)	124.8 (3)	C(7)–C(8)–C(9)	122.5 (3)
C(7)–C(8)–O(1)	120.3 (3)	C(9)–C(8)–C(1)	117.2 (3)
C(8)–C(9)–C(10)	120.5 (3)	C(9)–C(10)–C(11)	117.0 (3)
C(9)–C(10)–N(1)	120.5 (3)	C(11)–C(10)–N(1)	122.5 (3)
C(10)–C(11)–C(12)	121.3 (3)	C(7)–C(12)–C(11)	121.1 (3)
C(14)–C(13)–C(18)	116.6 (3)	C(14)–C(13)–N(3)	116.9 (3)
C(18)–C(13)–N(3)	126.5 (3)	C(13)–C(14)–C(15)	123.5 (3)
C(13)–C(14)–O(1)	120.5 (3)	C(15)–C(14)–C(1)	116.1 (3)
C(14)–C(15)–C(16)	120.3 (3)	C(15)–C(16)–C(17)	116.4 (3)
C(15)–C(16)–N(2)	121.3 (3)	C(17)–C(16)–N(2)	122.3 (3)
C(16)–C(17)–C(18)	122.2 (3)	C(13)–C(18)–C(17)	121.1 (3)
C(1)–C(19)–O(2)	120.3 (3)	C(1)–C(19)–N(3)	118.6 (3)
O(2)–C(19)–N(3)	121.1 (3)	C(21A)–C(20A)–N(1)	106.7 (5)
C(21B)–C(20B)–N(1)	108.7 (6)	C(23)–C(22)–N(1)	114.1 (4)
C(25)–C(24)–N(2)	114.3 (3)	C(27)–C(26)–N(2)	114.2 (3)
C(8)–O(1)–C(14)	114.2 (2)	C(10)–N(1)–C(20A)	119.8 (3)
C(10)–N(1)–C(20A)	117.6 (4)	C(20A)–N(1)–C(20B)	40.1 (3)
C(10)–N(1)–C(20B)	121.6 (3)	C(20A)–N(1)–C(22)	116.0 (3)
C(20B)–N(1)–C(22)	115.5 (3)	C(16)–N(2)–C(24)	121.3 (3)
C(16)–N(2)–C(26)	120.7 (3)	C(24)–N(2)–C(26)	117.6 (3)
C(7)–N(3)–C(13)	114.1 (3)	C(7)–N(3)–C(19)	122.9 (3)
C(13)–N(3)–C(19)	123.0 (3)		

The bond angles around atom C(19) are, as expected, all close to 120°. The relatively short length of C(1)–C(19) and C(19)–N(3) indicates that, despite the high value of torsional angle C(2)–C(1)–C(13)–N(3) [43 (1)°], delocalization operates between ring C(1)···C(6), the carbonyl group and the lone pair of electrons on N(3). C(7)–N(3) and C(13)–N(3) bonds are longer than C(19)–N(3), but are of comparable length to the C–N bonds within the *N,N*-diethyl groups, *e.g.* C(22)–N(1). C(8)–O(1) and C(14)–O(1) bonds are slightly shorter than the average C–O single bond, but longer than C–O bonds in delocalized systems [*e.g.* 1·355 (4) Å in CVL, Theocharis & Jones, 1984]. There should therefore be no appreciable delocalization between the three phenyl rings. The length of bonds C(10)–N(1) and C(16)–N(2) indicates the presence, as expected, of interaction between the lone pairs of electrons on N(1) and N(2) with rings C(7)···C(12) and C(13)···C(18), respectively. The C–N distances within the *N,N*-diethyls are of the correct magnitude for single bonds.

The lengths of C–N and C–C bonds in the disordered ethyl group are consistently higher than for the other three ethyls. This, however, may be compensated for by the higher e.s.d. values associated with these atoms. Disorder of ethyl groups, as a literature survey (using the Cambridge Crystallographic Database) of diethyl- and triethyl-phosphine bearing structures has indicated, is very common. The model used to describe the disorder varies from structure to structure, from the refinement of a single carbon atom

at two different positions to instances where the whole group was totally disordered. The low *R* achieved in this work indicates that the model used describes adequately the disorder present in this structure.

Ring $C(1)\cdots C(6)$ subtends a dihedral angle of 60 (1)° with ring $C(7)\cdots C(12)$ and 30 (1)° with ring $C(13)\cdots C(18)$, whilst the latter two rings subtend a dihedral angle of 33 (1)° between them. Ring N(3)—C(7)—C(8)—O(1)—C(14)—C(13) is only partly planar, with maximum deviation from the mean plane of 0·24 (2) Å, but with values for the associated torsional angles N(3)—C(13)—C(14)—O(1) and N(3)—C(7)—C(8)—O(1) of only −2·2 (5)°. This heterocyclic ring makes dihedral angles of 44 (1)° with $C(1)\cdots C(6)$, 17 (1)° with $C(7)\cdots C(12)$ and 16 (1)° with $C(13)\cdots C(18)$. The molecule as a whole, therefore, has, as expected, a quasi-propeller shape.

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8-Methyl-1,2,3,4,5,6,7,8-heptathiaphosphocan-8-sulfid, CH₃PS₈

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Abstract. $M_r = 302\cdot50$, monoclinic, $P2_1/c$, $a = 11\cdot809\ (3)$, $b = 7\cdot957\ (3)$, $c = 11\cdot678\ (3)$ Å, $\beta = 106\cdot85\ (2)°$, $V = 1050\cdot20$ Å³, $D_x = 1\cdot913$ Mg m⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu(\text{Mo } K\alpha) = 1\cdot720$ mm⁻¹, $F(000) = 608$, $T = 293$ K, $R_F = 0\cdot033$ for 1330 observed reflections $[\,|F_o| \geq 4\sigma(F_o)]$. The structure consists of a crown-like ring molecule, analogous to S_8, of seven S atoms and one P atom. To the latter another S atom is bonded in an equatorial and a methyl group in an axial position.

Einleitung. Verbindungen des Typs S_7X sind in grösserer Anzahl bekannt und auch an einigen Beispielen strukturell als kronenförmige Ringmoleküle charakterisiert worden [z.B. mit >S (Caron & Donohue, 1965; Abrahams, 1965; Sands, 1965); >S=O (Luger, Bradaczek, Steudel & Rebsch, 1976); >NH (Weiss & Neubert, 1965); >TeCl₂ (Weiss & Pupp, 1970)]. Ein wegen des Kovalenzradius des Phosphors dem S_8-Molekül in seinen Abmessungen vergleichbarer S_7P-Ring fehlte allerdings bisher. Diese Lücke konnte

inzwischen durch die Darstellung der Verbindung $S_7P(S)CH_3$ geschlossen werden, die aus $H_3CP(S)$-[SSi(CH₃)₃]₂ und S_5Cl_2 in Toluol unter Anwendung des Verdünnungsprinzips erhältlich ist und beim Umkristallisieren aus CS_2 in hellgelben, luftbeständigen, bei ungefähr 398 K unter Zersetzung schmelzenden rhombenartigen Säulen anfällt (Hahn & Nataniel, 1984). Wir haben dieses erste S_7P-Ringmolekül mit einer Methyl-phosphathian-Gruppe auch mit dem Ziel strukturell untersucht, die mit anderen Methoden nicht zugängliche Konfiguration des Moleküls im Festkörper zu ermitteln. Bei Raumtemperatur liegen nämlich die beiden Isomeren mit axialer und äquatorialer Stellung der Methylgruppe nach NMR-spektroskopischen Untersuchungen auf Grund der Ringinversion ungefähr äquimolar in Lösung vor, aus der aber nur ein Isomeres kristallisiert (Hahn, 1984).

Experimentelles. Schwach gelber, plättchenförmiger Kristall (~0,25 × 0,20 × 0,05 mm). CAD-4 Enraf–Nonius, Delft, Mo $K\alpha$-Strahlung, Graphit-