substituents, including the compound reported herein.

We thank M. J. Dylla, College of St. Catherine, for the synthesis of the title compound.

References

BIELUSHKIN, A. V., NATKANIEC, I., WASICKI, J., KHOMENKO, V. G., TELESHENKO, YU. & WASIUTYNSKI, T. (1986). 10th *European Crystallographic Meeting*, Wrocław, Poland. Collected Abstracts, 3A-05, pp. 350–351.

BRITTON, D. & GLEASON, W. B. (1991). *Acta Cryst.* C**47**, 2127–2131.

BROCK, C. P., KUO, M.-S. & LEVY, H. A. (1978). *Acta Cryst.* B**34**, 981–985.

BROCK, C. P. & MINTON, R. P. (1989). *J. Am. Chem. Soc.* **111**, 4586–4593.

CASALONE, G., MARIANI, C., MUGNOLI. A. & SIMONETTA, M. (1969). *Acta Cryst.* B**25**, 1741–1750.

Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KRONEBUSCH, P., GLEASON, W. B. & BRITTON, D. (1976*a*). *Cryst. Struct. Commun.* **5**, 17–20.

KRONEBUSCH, P., GLEASON, W. B. & BRITTON, D. (1976*b*). *Cryst. Struct. Commun.* **5**, 839–842.

LEMEE, H. M., TOUPET, L., DELUGEARD, Y., MESSAGER, J. C. & CAILLEAU, H. (1987). *Acta Cryst.* B**43**, 466–470.

MCNAMARA, J. M. & GLEASON, W. B. (1976). *J. Org. Chem.* **41**, 1071–1072.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*78. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Acta Cryst. (1991). C**47**, 2134–2137

Structure of 4-Dibenzofurancarboxaldehyde, $C_{13}H_8O_2$

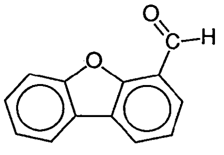
BY LAWRENCE J. FITZGERALD, JUDITH C. GALLUCCI, ROGER E. GERKIN* AND VIRESH H. RAWAL

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, *USA*

(*Received* 7 *December* 1990; *accepted* 13 *March* 1991)

Abstract. $M_r = 196{\cdot}21$, monoclinic, $P2_1/n$, $a = 6{\cdot}589\,(1)$, $b = 9{\cdot}784\,(2)$, $c = 14{\cdot}394\,(2)$ Å, $\beta = 95{\cdot}69\,(1)°$, $V = 923{\cdot}4\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\overline{\alpha}$) = 0·71073 Å, $\mu = 0{\cdot}89$ cm^{-1}, $F(000) = 408$, $T = 296$ K, $R = 0{\cdot}048$ for 964 unique reflections having $I > 3\sigma_I$. The average C—C bond length within the benzenoid rings in 4-dibenzofurancarboxaldehyde is 1·388 (9) Å; the average interior angle is 120·0 (2·6)°. While two of the three rings of 4-dibenzofurancarboxaldehyde are planar, the benzenoid ring to which the carbonyl group is attached is slightly non-planar. The dihedral angle between the two benzenoid rings measures 1·4(1)°. The structure is composed of pairs of 4-dibenzofurancarboxaldehyde molecules related by inversion centers. This structure is further characterized by approaches of both the carbonyl and the furan O atoms to ring H atoms with separations which are slightly less than the sum of the relevant van der Waals radii.

Introduction. In conjunction with continuing studies of positional disorder of the type displayed by dibenzofuran (Reppart, Gallucci, Lundstedt & Gerkin, 1984) interest has arisen in the structure of substituted dibenzofurans. This report presents an investigation of crystalline 4-dibenzofurancarboxaldehyde (I), whose structure had not previously been described.



(I)

Experimental. 4-Dibenzofurancarboxaldehyde (Gilman, Tolman, Yeoman, Woods, Shirley & Avakian, 1946) (I) was prepared by lithiation of dibenzofuran (Aldrich Chemical Company) with *sec*-butyllithium in tetrahydrofuran at 195 K followed by quenching with dimethylformamide. The crude product was purified by flash chromatography (Still, Kahn & Mitra, 1978), which produced an off-white powder. The 4-dibenzofurancarboxaldehyde was then sublimed under vacuum for 2 h at 353 K followed by continued sublimation for 2 days at

---

* To whom correspondence should be addressed.

room temperature. This sublimation process yielded the experimental sample, a clear rectangular prism with dimensions approximately 0·19 × 0·19 × 0·31 mm. The sample was mounted with epoxy cement on a glass fiber and analyzed at room temperature with a Rigaku AFC5S diffractometer utilizing monochromated Mo $K\bar{\alpha}$ radiation.

Unit-cell parameters were obtained from a symmetry-restricted least-squares fit of the setting angles for 25 centred reflections with $26 \leq 2\theta \leq 29°$. Intensity data were measured for 3065 reflections (exclusive of standards) with $+h$, $+k$, $\pm l$ indices ($h_{\max} = 9$, $k_{\max} = 13$, l -20 to 20) and 2θ values in the range $4 \leq 2\theta \leq 60°$. The ω–2θ scan technique was employed with scan widths $(1{\cdot}35 + 0{\cdot}35\tan\theta)°$ in ω and a background/scan time ratio of 0·5. A variance was assigned to each reflection by means of the formula $\sigma_I^2 = \sigma_{\rm cs}^2(I) + (0{\cdot}03I)^2$ in which $\sigma_{\rm cs}$ is based on counting statistics and I is the integrated intensity. Six standard reflections (121, 101, 022, $12\bar{7}$, 245, $16\bar{2}$) were measured after every 150 reflections; over the course of the intensity data collection they showed, on average, a relative intensity decay of 5·2%. A linear correction was applied to account for this decay. The data were corrected for Lorentz and polarization effects. An absorption correction was not required. Averaging equivalent reflections gave 2844 independent reflections with $R_{\rm int} = 0{\cdot}038$.

Among the primitive monoclinic space groups allowed by the data, the observed systematic absences ($0k0$, k = odd; $h0l$, $h + l$ = odd) uniquely determined the space group as $P2_1/n$ (No. 14). The direct-methods *MITHRIL* (Gilmore, 1984) program in the *TEXSAN* (Molecular Structure Corporation, 1989) structure analysis package was used to generate an E map from which the initial positions of all non-H atoms were identified. Difference Fourier synthesis methods were used to locate the positions of the H atoms. Full-matrix least-squares refinement was performed to minimize the function $\sum\sigma_F^{-2}(|F_o| - |F_c|)^2$ in which $\sigma_F = \sigma_I/2F{\rm Lp}$. Neutral atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for C and O; the scattering factor for H was taken from Stewart, Davidson & Simpson (1965). The non-H atoms were refined to the anisotropic stage using the data having $I > 3\sigma_I$; the H-atom positions were then identified and subsequently refined isotropically.

The results for the final refinement cycle were: 964 independent observations having $I > 3\sigma_I$; 168 variables; $R = 0{\cdot}048$; $wR = 0{\cdot}049$; $w = \sigma_F^{-2}$; $S = 1{\cdot}50$; $(\Delta/\sigma)_{\max} < 0{\cdot}01$. Max. and min. peaks on the final electron density difference map had values $+0{\cdot}22$ and $-0{\cdot}22$ e Å^{-3}, respectively. The max. peak was located at $x = 0{\cdot}65$, $y = 0{\cdot}37$, $z = 1{\cdot}04$, 1·4 Å from the least-squares plane of the molecule and approximately 1·5 Å from O2; the min. peak was located at $x = 0{\cdot}89$, $y = 0{\cdot}11$, $z = 0{\cdot}92$, near the least-squares plane of the molecule and approximately 1·2 Å from C10. [For the final refinement cycle for 1245 independent observations having $I > \sigma_I$: $R = 0{\cdot}069$; $wR = 0{\cdot}058$; $S = 1{\cdot}52$; $(\Delta/\sigma)_{\max} < 0{\cdot}01$. Similarly, for the final refinement cycle for 2048 independent observations having $I > 0$: $R = 0{\cdot}133$; $wR = 0{\cdot}065$; $S = 1{\cdot}30$; $(\Delta/\sigma)_{\max} < 0{\cdot}01$. These latter results are for comparison purposes only.]

Table 1. *Final positional parameters and isotropic and equivalent isotropic displacement parameters,* $B_{\rm eq}/B$ (Å^2), *for* 4-*dibenzofurancarboxaldehyde at* 296 K

E.s.d.'s are given within parentheses.

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}/B$
O1	0·7689 (3)	0·1331 (2)	0·9741 (1)	3·2 (1)
O2	0·7432 (5)	0·3132 (3)	1·1344 (2)	5·6 (2)
C1	1·2468 (5)	0·2268 (4)	0·8909 (2)	3·6 (2)
C2	1·3188 (6)	0·3245 (4)	0·9543 (3)	4·0 (2)
C3	1·2079 (6)	0·3615 (4)	1·0271 (3)	4·0 (2)
C4	1·0178 (5)	0·3043 (4)	1·0391 (2)	3·3 (2)
C6	0·6121 (5)	−0·0481 (4)	0·8735 (2)	3·4 (2)
C7	0·6364 (6)	−0·1279 (4)	0·7961 (2)	3·8 (2)
C8	0·8072 (5)	−0·1154 (4)	0·7470 (2)	3·9 (2)
C9	0·9591 (6)	−0·0232 (4)	0·7733 (2)	3·6 (2)
C10	0·9380 (5)	0·0598 (3)	0·8510 (2)	2·8 (1)
C11	0·7654 (5)	0·0440 (3)	0·8984 (2)	2·9 (1)
C12	0·9498 (5)	0·2044 (3)	0·9744 (2)	2·9 (1)
C13	1·0599 (5)	0·1643 (3)	0·9011 (2)	2·8 (1)
C14	0·9089 (7)	0·3499 (4)	1·1180 (3)	4·4 (2)
H1	1·329 (4)	0·200 (3)	0·839 (2)	4·0 (8)
H2	1·454 (5)	0·370 (3)	0·951 (2)	4·4 (8)
H3	1·258 (5)	0·431 (3)	1·071 (2)	3·5 (8)
H6	0·499 (5)	−0·056 (3)	0·908 (2)	3·8 (8)
H7	0·533 (5)	−0·194 (3)	0·778 (2)	3·4 (8)
H8	0·816 (5)	−0·173 (3)	0·691 (2)	3·9 (8)
H9	1·075 (5)	−0·011 (3)	0·739 (2)	3·3 (7)
H14	0·980 (6)	0·420 (4)	1·161 (3)	6·1 (10)

Discussion. The final atomic coordinates and equivalent isotropic and isotropic displacement parameters with their uncertainties are given in Table 1.* Since in this structure the asymmetric unit is an entire 4-dibenzofurancarboxaldehyde molecule there are no symmetry constraints linking any sets of distances or angles in the molecule.

Fig. 1 shows two 4-dibenzofurancarboxaldehyde molecules related by a center of inversion, with bond lengths and bond angles specified. The average C—C bond length within the two benzenoid rings is 1·388 (9) Å, typical of the average values for the benzenoid rings found in dibenzofuran [1·392 (7) Å; Reppart, Gallucci, Lundstedt & Gerkin, 1984],

---

* Lists of structure factors, anisotropic thermal parameters and data pertaining to least-squares best-fit planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54091 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

fluorene [1·388 (9) Å; Gerkin, Lundstedt & Reppart, 1984] and carbazole [1·388 (4) Å; Gerkin & Reppart, 1986]. The average interior angle for the two benzenoid rings is 120·0 (2·6)°, with C3—C4—C12 and C7—C6—C11 considerably smaller than 120° and with C4—C12—C13 and C6—C11—C10 considerably larger than 120°. This pattern is present also in dibenzofuran and carbazole, but not in fluorene. The two benzenoid rings have near *C*2 symmetry with a pseudo-twofold axis passing through O1 and lying in the plane of the molecule. The C—C bond lengths related in this manner agree within three times their e.s.d.'s except for the pairs C3—C4:C7—C6 and C4—C12:C6—C11. Here the bond lengths which involve C4, to which the carbonyl group is attached, are greater than the corresponding bond lengths in the other benzenoid ring. All the interior angles of the benzenoid rings related by the pseudo *C*2 symmetry agree within three times their e.s.d.'s.

The furan ring and the benzenoid ring involving C6–C11 are individually planar, the mean deviation of atoms from the best least-squares plane and χ^2 being, respectively, 0·003 (3) Å and 6·9, and 0·002 (1) Å and 7·4. The benzenoid ring involving C1–C4, C12, C13 and to which the carbonyl group is attached is slightly, but significantly, non-planar: the mean deviation of atoms from the best least-squares plane is 0·005 (4) Å and $\chi^2 = 19{\cdot}2$. This ring is twisted about an axis connecting C2 and C12, presumably due to the carbonyl group attached to C4. Additionally, the two benzenoid rings and the furan ring are not co-planar, the dihedral angle between the best least-squares planes of the two benzenoid rings being 1·4 (1)°; this result is again analogous to corresponding results for dibenzofuran, fluorene and carbazole. The carbonyl C atom, C14, is in the plane of the benzenoid ring to which it is attached, within one e.s.d. However, the carbonyl O atom, O2, and H atom, H14, deviate from the ring plane by −0·065 (4) and +0·04 (4) Å respectively. Consequently, there is a dihedral angle of 3·2 (7)° between the plane of the carbonyl group and the associated ring plane.

Fig. 2 presents a stereoview of the unit cell showing the four molecules whose major portions are within the cell together with ten additional molecules. The view illustrates how the 4-dibenzofurancarboxaldehyde molecules are related across inversion centers as well as how they stack. Fig. 1 depicts specific inter- and intramolecular close approaches (dashed lines) that are attendant upon this arrangement. The carbonyl O atom is involved in two such approaches, O2···H7^{i}, 2·59 (3) Å, and O2···O1, 2·92 (1) Å, the magnitudes of which are slightly less than the sum of the relevant van der Waals radii (Bondi, 1964). The furan O atom is also involved in a third close approach, O1···H6^{i}, 2·68 (3) Å, whose magnitude is also slightly less than the sum of van der Wals radii. The H14···H3 interaction, the distance between the atoms being 2·35 (5) Å, tends to prevent in-plane deformation that might relieve this crowding while crystal packing tends to prevent any further out-of-plane deformation.

The close packing is consistent with the absence of any observable disorder of the type found in dibenzofuran (Reppart, Gallucci, Lundstedt & Gerkin, 1984).

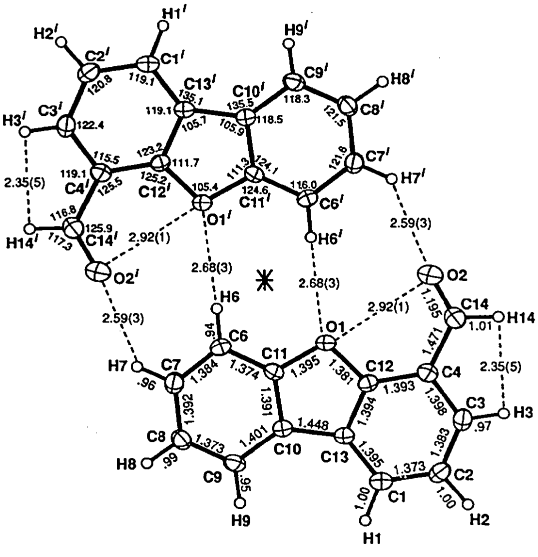


Fig. 1. An illustration of two 4-dibenzofurancarboxaldehyde molecules related by an inversion center as determined in this research, prepared using *ORTEP*II (Johnson, 1976), and showing labeling of atoms, distances (Å) and angles (°). The uncertainty for bond lengths involving atoms other than H is ≤0·005 Å, for H atoms ≤ 0·03 Å. The uncertainty for angles involving atoms other than H is ≤ 0·4°, for angles involving H atoms ≤ 2°. Intra- and intermolecular distances (Å) of closest approach are shown by the dashed lines. Thermal ellipsoids are drawn at 25% probability for all atoms except H, for which they have been set artificially small. The asterisk denotes the inversion center.

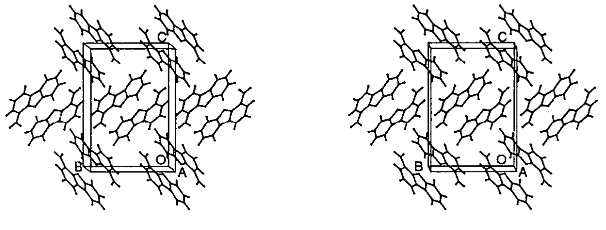


Fig. 2. Stereoview of a portion of the 4-dibenzofurancarboxaldehyde crystal, including a unit cell, prepared using *ORTEP*II (Johnson, 1976). The four molecules whose major portions are in the unit cell are shown along with ten other molecules.

The support of LJF by PPG Industries is gratefully acknowledged. We thank a referee for helpful comments. Partial support of this research through the purchase of the diffractometer system by an NIH grant is also gratefully acknowledged.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Gerkin, R. E., Lundstedt, A. P. & Reppart, W. J. (1984). *Acta Cryst.* C**40**, 1892–1894.

Gerkin, R. E. & Reppart, W. J. (1986). *Acta Cryst.* C**42**, 480–482.

Gilman, H., Tolman, L., Yeoman, F., Woods, L. A., Shirley, D. A. & Avakian, S. (1946). *J. Am. Chem. Soc.* **68**, 426–428.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*, Version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

Reppart, W. J., Gallucci, J. C., Lundstedt, A. P. & Gerkin, R. E. (1984). *Acta Cryst.* C**40**, 1572–1576.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.

Still, W. C., Kahn, M. & Mitra, A. (1978). *J. Org. Chem.* **43**, 2923–2925.

Acta Cryst. (1991). C**47**, 2137–2141

Structures of Photochromic Spiroindolinobenzoxazines and a Spiroindolinobenzopyran

By Yasuko T. Osano, Kazuo Mitsuhashi, Shuichi Maeda and Takao Matsuzaki

Research Center, Mitsubishi Kasei Corporation, Kamoshida, Midoriku, Yokohama 227, *Japan*

(*Received* 22 *November* 1990; *accepted* 18 *March* 1991)

Abstract. The crystal structures of two photochromic spirooxazines and a related spiropyran have been determined by X-ray crystallographic techniques. Crystal data are: 1-(2-methoxyethyl)-3,3,5-trimethylspiro[indoline-2,2′-[2*H*]-naphtho[2,1-*b*][1,4]oxazine] (1), $C_{25}H_{26}N_2O_2$, M_r = 386·5, orthorhombic, $P2_12_12_1$, a = 10·913 (3), b = 18·603 (4), c = 10·231 (3) Å, V = 2077 Å^3, Z = 4, D_m (flotation) = 1·25, D_x = 1·236 g cm^{-3}, Cu $K\alpha$, λ = 1·5418 Å, μ = 5·85 cm^{-1}, $F(000)$ = 824, T = 296 K, R = 0·064 for 2040 reflections with $|F| \geq \sigma(|F|)$; 1-(2-methoxyethyl)-3,3-dimethylspiro[indoline-2,2′-[2*H*]-pyrido[3,2-*f*][1,4]-benzoxazine] (2), $C_{23}H_{23}N_3O_2$, M_r = 373·5, monoclinic, $P2_1/c$, a = 22·029 (2), b = 10·885 (1), c = 17·549 (1) Å, β = 96·27 (1)°, V = 4182·8 Å^3, Z = 8, D_m (flotation) = 1·26, D_x = 1·186 g cm^{-3}, Cu $K\alpha$, λ = 1·5418 Å, μ = 5·80 cm^{-1}, $F(000)$ = 1584, T = 296 K, R = 0·065 for 7001 reflections with $|F| \geq \sigma(|F|)$; 1-(2-methoxyethyl)-3,3,5-trimethylspiro[indoline-2,2′-[2*H*]-naphtho[2,1-*b*]pyran] (3), $C_{26}H_{27}NO_2$, M_r = 385·5, monoclinic, $P2_1/c$, a = 19·271 (1), b = 6·764 (1), c = 16·302 (3) Å, β = 96·27 (1)°, V = 2112·2 Å^3, Z = 4, D_m (flotation) = 1·18, D_x = 1·213 g cm^{-3}, Cu $K\alpha$, λ = 1·5418 Å, μ = 5·60 cm^{-1}, $F(000)$ = 824, T = 296 K, R = 0·072 for 4035 reflections with $|F| \geq \sigma(|F|)$. The distances of the C_{spiro}—O bond which cleaves on photoreaction are similar in the three compounds but the C_{spiro}—N bond distance in the spiropyran is longer than those in the spirooxazines. The spiropyran also has the strongest intramolecular short contacts compared with spirooxazines. These structural differences suggest that an unstable photoproduct is the reason why the spiropyran shows photochromism only at low temperatures.

Introduction. While photochromic spiroindolinobenzopyrans have been extensively studied (Tyer & Becker, 1970*a*,*b*; Aldoshin, Atovmyan, D'yachenko & Gal'bershtam, 1981; Aldoshin & Atovmyan, 1984, 1987; Aldoshin, Atovmyan & Kozina, 1986, 1987*a*,*b*) only a few spectral and structural studies (Chu, 1983; Clegg, Norman, Lasch & Kwak, 1987; Clegg, Norman, Flood, Sallans, Kwak, Kwiatkowski & Lasch, 1991) have been reported for spiroindolinobenzoxazines. Spirooxazines are useful compounds because they show greater durability than spiropyrans on repeated photochromic reactions. Structural information seems to be important for understanding the photochromic properties and mechanisms of the photocolouration. The present paper describes the crystal structures of spiroindolinobenzoxazines, (1) and (2), and a related spiroindolinobenzopyran (3). (1) and (3) have similar

0108-2701/91/102137-05$03.00