pseudo-Azulenes. Part 7.[1] Crystal and Molecular Structure of Benzo[*b*]indeno[1,2-*e*]pyran

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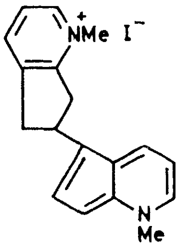
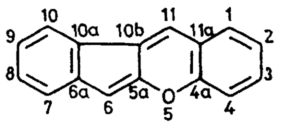
X-Ray diffraction of the title compound shows that the molecule is planar. The bond lengths of the central cyclopenta[*b*]pyran system indicate pronounced bond alternation and hence little aromatic character. The results of ωβ-calculations are in good agreement with the experimental bond distances.

HETEROCYCLIC systems iso-π-electronic with azulene have been studied extensively during the past twenty years.[2] Numerous chemical, physicochemical, and theoretical investigations stress the qualitative similarity of these compounds to azulene, and it appears that replacement of a C=C unit in the seven-membered ring of azulene by a heteroatom capable of contributing two π-electrons maintains the character of the parent molecule. The aromaticity of azulene is most convincingly demonstrated by the lengths of its peripheral bonds, mean 1.40 Å, thus showing extensive delocalization of the ten π-electrons.[3] In contrast, the transannular link is long, 1.48—1.52 Å in azulene and its derivatives, indicating that the molecule is best represented as a [10]annulene with an essentially single bridging bond. It is of interest to compare the geometry of azulene with those of its heteroanalogues, but to date only one structure of a *pseudo*-azulene has been determined, namely that of the derivative (1) of cyclopenta[*b*]pyridine.[4] The carbon–carbon bonds in the cyclopentapyridine moiety of this molecule, which is planar, vary from 1.340 to 1.392 Å [double bonds in formula (1)] and 1.403 to 1.450 Å (single bonds); these distances, together with the length (1.482 Å) of the transannular bond, led the authors to conclude that the compound was essentially azulenoid and hence aromatic. In order to gain further insight into the electronic structure of *pseudo*-azulenes, we have determined the crystal structure of benzo[*b*]indeno[1,2-*e*]pyran (2),[5] an oxygen analogue of azulene.



(1)



(2)

EXPERIMENTAL

The title compound (2) was recrystallized from toluene as dark red, acicular crystals, m.p. 176—177 °C. Weissenberg and precession photographs showed that the crystals were orthorhombic, with space group either $Pca2_1$ or *Pcam*. Accurate unit-cell dimensions were obtained by a weighted (w = tan θ) least-squares fit to the θ-values of 20 high-angle reflexions measured on a Siemens four-circle single-crystal diffractometer (AED) with Cu-*K* radiation (α_1 = 1.540 51, α_2 = 1.544 34, $\bar{\alpha}$ = 1.5418 Å).

Crystal Data.—$C_{16}H_{10}O$, M_r = 218.26. Orthorhombic, a = 22.474 3(26), b = 5.865 7(7), c = 16.431 9(19) Å, U = 2 166.2(4) Å^3, D_m = 1.34(1) (by flotation in aqueous sodium iodide), D_c = 1.338 3(2) g cm^{-3}, $F(000)$ = 912. μ(Cu-K_α) = 7.8 cm^{-1}. Space group $Pca2_1$.

Intensity Data.—A crystal of dimensions 0.25 × 0.15 × 0.15 mm, parallel to *a*, *b*, and *c*, respectively, was selected for intensity measurements. The intensities of 2 017 symmetry-independent reflexions with λ^{-1} sinθ < 0.61 were measured on a diffractometer, equipped with a scintillation counter and pulse-height discriminator, by the five-value technique.[6] A reference reflexion, monitored after every 20 intensities measured, gave no indication of crystal decomposition. The data were scaled, and each intensity was assigned a variance, $\sigma^2(I)$, based on counting statistics. A total of 423 reflexions with $I/\sigma(I) < 2.58$ was classified as unobserved. Lorentz and polarization, but not absorption, corrections were applied.

Structure Determination and Refinement.—The structure was solved, with difficulty, by direct methods, during which work the space group was established as $Pca2_1$. $|E|$-Values were calculated by a modified *K*-curve method,[7] and input to the MULTAN program.[8] The heavy atoms of one complete molecule and part of the second in the asymmetric unit were obtained from the best *E* map. The remaining heavy atom positions were obtained by conventional Fourier techniques.

Hydrogen atoms were located by difference-Fourier techniques, and all atoms were refined by weighted least-squares, the heavy atoms with anisotropic and the hydrogen atoms with isotropic temperature factors, to convergence at *R* 0.046. An analysis of $w(|F_o| - |F_c|)^2$ in ranges of $|F_o|$ confirmed the suitability of the weighting function. Atomic scattering factors were taken from ref. 9 and the *XRAY*-72 '76 programs,[10] at the University of London Computer Centre, were used to supplement local facilities. Structure factors and thermal parameters are deposited in Supplementary Publication No. SUP 22358 (20 pp., 1 microfiche).†

DISCUSSION

Description of the Structure.—The atomic co-ordinates are listed in Table 1, bond lengths and bond orders in Table 2, and bond angles in Table 3. The two molecules in the asymmetric unit are situated athwart an approximate, non-crystallographic centre of symmetry, as shown in the packing diagram (Figure). This feature was responsible for the difficulty in solving the structure.

The terminal benzene rings are planar, and the mole-

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† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

cule, as a whole, is planar to within <5°. In the asymmetric unit, the angle between the mean planes of the two molecules is only 1°. In the packing diagram, we can identify the left- and right-hand and middle sheets of molecules. If the outer sheets were moved along *a* to bring the pseudo-centre on to the screw axis, and the middle sheet moved along $-a$ to preserve the *c*-glide, space group *Pcam* would be produced. The actual structure can be regarded as an energetically favourable collapse from the awkward and wasteful packing of *Pcam*. The geometry of the two independent molecules shows good agreement; there exists some correlation between molecules (1) and (2) in the least-squares calculations. There are no significant contact distances <3.6 Å, and, hence, no indications of hydrogen bonding.

TABLE 1

Fractional co-ordinates of atoms ($\times 10^4$, for H atoms $\times 10^3$), with estimated standard deviations in parentheses

	x	*y*	*z*
(*a*) Molecule (1)			
C(1)	2 409(2)	465(9)	2 062(3)
C(2)	1 881(2)	1 077(11)	2 460(3)
C(3)	1 614(2)	3 189(11)	2 298(3)
C(4)	1 860(2)	4 657(9)	1 741(3)
C(4a)	2 382(2)	4 088(8)	1 358(3)
O(5)	2 600(1)	5 664(5)	820 *
C(5a)	3 095(2)	5 095(8)	368(3)
C(6)	3 364(2)	6 383(8)	−209(3)
C(6a)	3 880(2)	5 057(8)	−502(3)
C(7)	4 307(2)	5 571(8)	−1 086(3)
C(8)	4 737(2)	3 959(9)	−1 236(3)
C(9)	4 766(2)	1 890(8)	−811(3)
C(10)	4 341(2)	1 374(8)	−231(3)
C(10a)	3 892(2)	2 963(7)	−77(3)
C(10b)	3 396(2)	2 936(7)	489(3)
C(11)	3 198(2)	1 412(8)	2(3)
C(11a)	2 666(2)	1 997(7)	1 495(3)
(*b*) Molecule (2)			
C(1)	1 303(2)	4 238(9)	−522(3)
C(2)	1 840(2)	3 629(9)	894(3)
C(3)	2 103(2)	1 590(9)	−696(3)
C(4)	1 836(2)	89(9)	−141(3)
C(4a)	1 304(2)	752(8)	220(3)
O(5)	1 065(1)	−777(5)	782(2)
C(5a)	569(2)	−148(7)	1 190(3)
C(6)	281(2)	−1 367(8)	1 768(3)
C(6a)	−223(2)	−19(8)	2 032(3)
C(7)	−661(2)	−409(8)	2 601(3)
C(8)	−1 099(2)	1 240(9)	2 743(3)
C(9)	−1 106(2)	3 258(9)	2 299(3)
C(10)	−676(2)	3 701(8)	1 715(3)
C(10a)	−236(2)	2 058(7)	1 583(2)
C(10b)	272(2)	2 008(7)	1 036(2)
C(11)	489(2)	3 463(7)	474(3)
C(11a)	1 026(2)	2 849(8)	35(3)
(*c*) Hydrogen atoms molecule (1)			
H(1)	262	−108	219
H(2)	168	−13	287
H(3)	123	362	257
H(4)	166	621	162
H(6)	324	793	−46
H(7)	431	710	−141
H(8)	504	430	−168
H(9)	510	77	−96
H(10)	435	−20	6
H(11)	342	−15	113
(*d*) Hydrogen atoms molecule (2)			
H(1)	110	580	−65
H(2)	203	468	−132
H(3)	249	117	−98
H(4)	203	−151	−2
H(6)	40	−299	196
H(7)	−66	−191	291
H(8)	−143	91	315
H(9)	−141	450	242
H(10)	−68	516	137
H(11)	27	497	34

* Invariant co-ordinate.

TABLE 2

Bond lengths (Å) and bond orders

	Molecule (1)	Molecule (2)	Mean	Bond order (p_{rs})
C(1)–C(2)	1.400(7)	1.398(7)	1.399(7)	0.698
C(1)–C(11a)	1.418(7)	1.375(6)	1.397(7)	0.593
C(2)–C(3)	1.402(8)	1.373(7)	1.388(8)	0.635
C(3)–C(4)	1.374(8)	1.403(7)	1.389(8)	0.680
C(4)–C(4a)	1.372(6)	1.390(6)	1.381(6)	0.640
C(4a)–O(5)	1.369(5)	1.395(5)	1.382(5)	
C(4a)–C(11a)	1 401(6)	1 413(6)	1 407(6)	0.586
O(5)–C(5a)	1 379(5)	1 352(5)	1 366(6)	
C(5a)–C(6)	1.355(6)	1.354(6)	1.355(6)	0.815
C(5a)–C(6)	1 355(6)	1.354(6)	1.355(6)	0.815
C(5a)–C(10b)	1.449(6)	1.452(6)	1.451(6)	0.377
C(6)–C(6a)	1.478(6)	1.447(6)	1.463(6)	0.412
C(6a)–C(7)	1.390(6)	1.377(6)	1.384(6)	0.610
C(6a)–C(10a)	1.413(6)	1.424(6)	1.419(6)	0.567
C(7)–C(8)	1.376(7)	1.400(7)	1.388(7)	0.686
C(8)–C(9)	1.402(7)	1.391(7)	1.397(7)	0.638
C(9)–C(10)	1.383(6)	1.386(6)	1.385(6)	0.680
C(10)–C(10a)	1.397(6)	1.398(6)	1.398(6)	0.626
C(10a)–C(10b)	1.451(6)	1.453(5)	1.452(6)	0.366
C(10b)–C(11)	1.356(6)	1.349(6)	1.353(6)	0.783
C(11)–C(11a)	1.445(6)	1.451(6)	1.448(6)	0.434

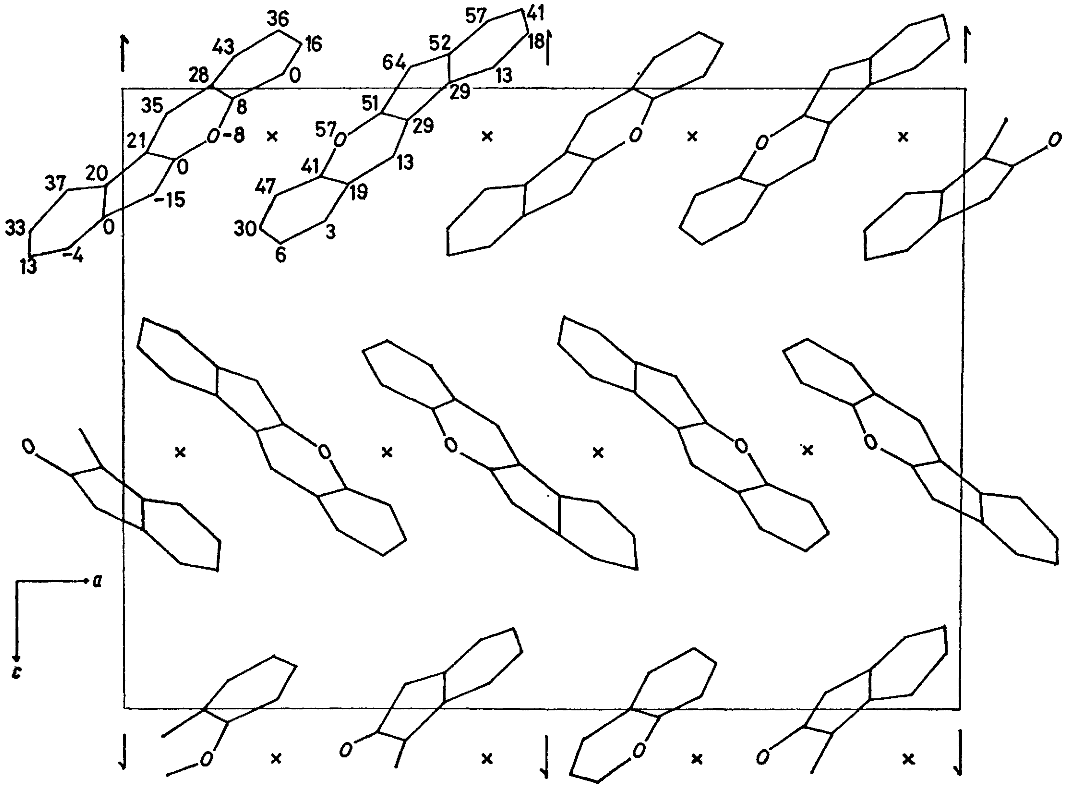
TABLE 3

Bond angles (°)

	Molecule (1)	Molecule (2)	Mean
C(2)–C(1)–C(11a)	119.4(5)	122 0(4)	120.7(5)
C(1)–C(2)–C(3)	120.0(5)	119.4(5)	119.7(5)
C(2)–C(3)–C(4)	120.5(6)	121.1(4)	120.8(5)
C(3)–C(4)–C(4a)	119.9(5)	118.0(4)	119.0(5)
C(4)–C(4a)–O(5)	116.0(4)	115.7(4)	115.9(4)
C(4)–C(4a)–C(11a)	121.9(4)	122.2(4)	122.1(4)
O(5)–C(4a)–C(11a)	122.1(4)	122.1(4)	122.1(4)
C(4a)–O(5)–C(5a)	118.2(3)	118.1(3)	118.2(3)
O(5)–C(5a)–C(6)	127.0(4)	126.8(4)	126.9(4)
C(5)–C(5a)–C(10b)	120.9(4)	122.0(4)	121.5(4)
C(6)–C(5a)–C(10b)	112.1(4)	111 2(4)	111.7(4)
C(5)–C(6)–C(6a)	106.5(4)	107.2(4)	106.9(4)
C(6)–C(6a)–C(7)	120.7(4)	132.2(4)	131.5(4)
C(6)–C(6a)–C(10a)	108.2(4)	109.2(4)	108.7(4)
C(7)–C(6a)–C(10a)	121.1(4)	118.6(4)	119.9(4)
C(6a)–C(7)–C(8)	117.4(4)	120.1(4)	118.8(4)
C(7)–C(8)–C(9)	122.6(4)	120.6(4)	121.6(4)
C(8)–C(9)–C(10)	120.0(4)	121.0(4)	120.5(4)
C(9)–C(10)–C(10a)	118.6(4)	118.1(4)	118.4(4)
C(6a)–C(10a)–C(10)	120.2(4)	121.6(4)	120.9(4)
C(6a)–C(10a)–C(10b)	108.2(4)	106.7(3)	107.5(4)
C(10)–C(10a)–C(10b)	131.6(4)	131.7(4)	131.7(4)
C(5a)–C(10b)–C(10a)	105.1(3)	105.7(3)	105.4(3)
C(5a)–C(10b)–C11(	121.1(4)	102.3(4)	120.7(4)
(10a)–C(10b)–C(11)	133.8(4)	134.0(4)	133.9(4)
C(10b)–C(11)–C(11a)	117.3(4)	118.9(4)	118.1(4)
C(1)–C(11a)–C(4a)	118.3(4)	117.3(4)	117.8(4)
C(1)–C(11a)–C(11)	121.5(4)	124.1(4)	122.8(4)
C(4a)–C(11a)–C(11)	120.2(4)	118.6(4)	119.4(4)

Bonding.—Little need be said about the bonds in the annelated benzene rings. Except at the ring junctions, they are not significantly (3σ) different from the standard [11] aromatic carbon–carbon bond length of 1.394 Å. The two C–O bond lengths are 1.366 and 1.382 Å.

Similar values (1.37 and 1.38 Å) were found for the structure of 2,6-dimethylpyran-4-thione.[12] They are considered to be normal for this class of compound, and the fact that their lengths are shorter than that for the saturated heterocyclic C–O (1.426 Å) indicates a certain degree of conjugation with the C(5a) and C(10b) double bonds, which are themselves longer (1.355 and 1.353 Å) than the standard C=C bond length (1.335 Å).



Packing of the molecules, as seen along b; numbers are $100xy$

The lengths of the carbon–carbon bonds in the central portion of the molecule are of greatest interest. They alternate strongly between essentially double bonds (1.354 Å) and single bonds (1.448 to 1.463 Å) between sp^2-hybridised carbon atoms, the alternation being more pronounced than in the case of the nitrogen analogue (1). In both molecules the transannular bond is long and, hence, essentially single. We conclude that the bond lengths in the cyclopentapyran derivative (2), while showing a certain degree of π-electron delocalization, indicate that the molecule is best represented by formula (2) and that it possesses little aromatic character. The bond distances in the series azulene, cyclopenta(b)-pyridine, and cyclopenta[b]pyran show that the aromaticity of the molecules decreases in this order, as predicted[13] by simple molecular orbital theory.

In conclusion, we report the results of bond-length calculations by a simple SCF–LCAO method, the $\omega\beta$-technique.[14] For planar molecules, this method depends solely on a choice of the Coulomb integral for any hetero-atom present. In the present case, h was varied from 0.5 to 2.5 in steps of 0.5, and it was found that the least standard deviation resulted for h 2.0, the value recommended by Streitwieser;[15] Table 2 lists the results. The regression line is $R_{rs} = 1.546 - 0.237p_{rs}$, where R_{rs} is the distance between carbon atoms r and s and p_{rs} the corresponding bond-order. This equation compares with that, $R_{rs} = 1.524 - 0.194\ p_{rs}$, obtained[14] for benzenoid hydrocarbons, and that, $R_{rs} = 1.517 - 0.180\ p_{rs}$, derived by Coulson and Gołebiewski.[16] Our equation yields a bond-length standard deviation σ of 0.030 Å, which is five times the mean standard deviation of the bond lengths found from the structure analysis.

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