Acta Cryst. (1977). B**33**, 3219–3221

syn-1,6:8,13-Biscarbonyl[14]annulene

By Riccardo Destro and Massimo Simonetta

Istituto di Chimica Fisica e Centro CNR, Università, Via Golgi 19, 20133 *Milano, Italy*

(*Received* 22 *February* 1977; *accepted* 31 *March* 1977)

Abstract. $C_{16}H_{10}O_2$, m.p. > 200°C (dec.), monoclinic, $P2_1/n$; $a = 9{\cdot}097$ (1), $b = 12{\cdot}764$ (1), $c = 9{\cdot}822$ (1) Å, $\beta = 94{\cdot}69$ (1)°, $V = 1136{\cdot}7$ Å^3; $M_r = 234{\cdot}3$, $Z = 4$, $D_c = 1{\cdot}369$, $D_m = 1{\cdot}362$ g cm^{-3} (flotation in dilute K_2HgI_4 solution). Computer-controlled four-circle diffractometer data (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, graphite monochromator), $F(000) = 488$, μ(Mo $K\alpha$) = $0{\cdot}97$ cm^{-1}, $t = 18 \pm 2$°C. The structure has been solved by direct methods and refined to an R of 0·040 for 2531 reflexions with $I > 0$. Comparison of the ring conformation with that of other *syn*-bridged [14]annulenes shows that the strain imposed by the two carbonyl groups affects torsion and bond angles much more than bond lengths.

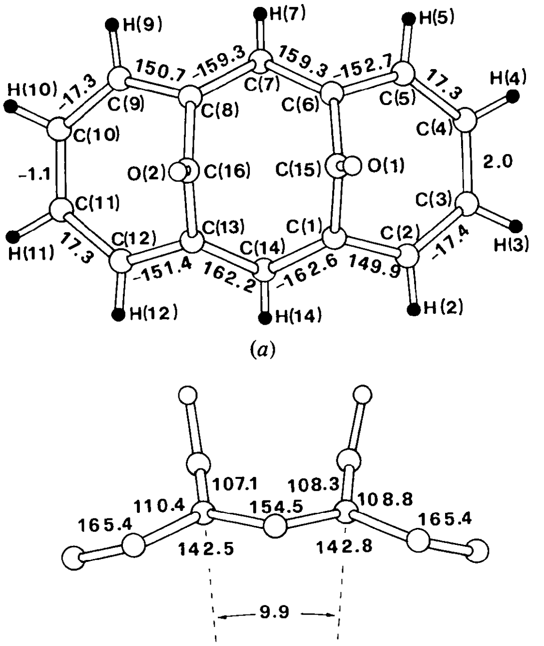


Fig. 1. The molecule of BCA viewed along a principal axis of inertia. (*a*) Numbering scheme and torsional angles along the annulene perimeter. (*b*) Dihedral angles between least-squares planes.

Table 1. *Final atomic coordinates and* (*in parentheses*) *standard deviations*

Fractional coordinates are $\times 10^5$ for C and O, $\times 10^4$ for H. Isotropic B's are $\times 10$.

	x	y	z
C(1)	61297 (11)	423 (8)	28159 (10)
C(2)	71398 (13)	−6814 (9)	23386 (14)
C(3)	80461 (14)	−4813 (11)	13133 (14)
C(4)	79385 (13)	3174 (11)	3190 (14)
C(5)	69327 (13)	11217 (10)	1310 (12)
C(6)	60058 (12)	14750 (8)	11176 (11)
C(7)	46344 (13)	19540 (8)	8539 (11)
C(8)	35852 (12)	19872 (8)	18107 (11)
C(9)	20572 (13)	21535 (9)	15112 (12)
C(10)	9641 (13)	17684 (10)	22619 (13)
C(11)	10231 (13)	9546 (11)	32327 (13)
C(12)	21997 (13)	3175 (11)	36694 (13)
C(13)	36846 (11)	5358 (8)	34784 (10)
C(14)	48027 (12)	−1950 (8)	33578 (11)
C(15)	65398 (10)	11425 (8)	25235 (10)
C(16)	39664 (10)	16664 (8)	32506 (10)
O(1)	73489 (8)	16645 (6)	32883 (8)
O(2)	43626 (9)	22673 (6)	41588 (8)

	x	y	z	B (Å^2)
H(2)	7105 (16)	−1356 (11)	2713 (14)	54 (3)
H(3)	8768 (17)	−1017 (12)	1137 (15)	58 (3)
H(4)	8601 (17)	235 (12)	−437 (16)	64 (4)
H(5)	6788 (15)	1467 (11)	−777 (14)	55 (3)
H(7)	4306 (13)	2125 (10)	−87 (12)	43 (3)
H(9)	1749 (14)	2540 (10)	669 (13)	47 (3)
H(10)	−73 (17)	2019 (11)	1965 (14)	58 (3)
H(11)	73 (17)	749 (11)	3549 (15)	60 (3)
H(12)	2021 (15)	−342 (11)	4148 (14)	55 (3)
H(14)	4590 (14)	−925 (10)	3512 (12)	43 (3)

Introduction. The conformation of bridged [14]annulenes with an anthracene perimeter has long been a subject of interest in our laboratory (Destro, Pilati & Simonetta, 1977; and references therein). As part of a systematic study of this class of substances we have undertaken the crystal structure analysis of the title compound (hereinafter BCA), recently synthetized, after considerable effort, by Vogel & Balci (1976).

Accurate cell dimensions were obtained by the fitting of $\sin^2\theta$ values of 75 reflexions. Systematic absences $h0l$ with $h + l$ odd and $0k0$ with k odd indicate the space group $P2_1/n$. Intensities were collected by the variable-rate θ–2θ scan technique on a Syntex $P\bar{1}$ diffractometer to a maximum 2θ value of 55°, using a crystal which had been ground to a sphere of approximate radius 0·2 mm. Background measurements were taken at both ends of the scan range, each

Table 2. *Bond lengths* (Å)

C(1)–C(2)	1·410 (2)	C(14)–C(1)	1·392 (2)
C(5)–C(6)	1·410 (2)	C(6)–C(7)	1·394 (2)
C(8)–C(9)	1·413 (2)	C(7)–C(8)	1·394 (2)
C(12)–C(13)	1·407 (2)	C(13)–C(14)	1·392 (2)
C(2)–C(3)	1·377 (2)	C(1)–C(15)	1·487 (1)
C(4)–C(5)	1·378 (2)	C(15)–C(6)	1·488 (2)
C(9)–C(10)	1·376 (2)	C(8)–C(16)	1·486 (2)
C(11)–C(12)	1·384 (2)	C(16)–C(13)	1·486 (1)
C(3) C(4)	1·410 (2)	C(15) O(1)	1·208 (1)
C(10)–C(11)	1·408 (2)	C(16)–O(2)	1·209 (1)
C(2)–H(2)	0·94 (1)	C(9)–H(9)	0·98 (1)
C(3)–H(3)	0·97 (2)	C(10)–H(10)	1·02 (2)
C(4)–H(4)	1·00 (2)	C(11)–H(11)	0·98 (2)
C(5)–H(5)	0·99 (1)	C(12)–H(12)	0·98 (1)
C(7)–H(7)	0·97 (1)	C(14)–H(14)	0·97 (1)

for a time equal to one-half the scan time. Two standard reflexions were checked after every 50 intensity measurements; they showed no appreciable trend. 2626 unique reflexions were measured, of which 2533 were treated as observed, with $I > 0$. Each reflexion was assigned a variance of $\sigma^2(I) = \sigma^2(I)_{\text{c.s.}} + (0{\cdot}03S)^2$, where S is the scan count. The intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods; the positions of all non-hydrogen atoms were derived from an E map and those of the H atoms were initially assumed at calculated positions. A modified version of *ORFLS* (Busing, Martin & Levy, 1962) was used for the full-matrix least-squares refinement by minimization of the quantity $\sum w(|F_o| - |F_c|)^2$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$, except for the 93 reflexions having $I < 0$, for which $w = 0$. Two of the strongest reflexions, 021 and 110, presumably suffering from counting losses, were also excluded from the refinement. In the final cycles, 204 parameters were simultaneously adjusted: coordinates and anisotropic temperature coefficients, b_{ij}, for the 18 heavy atoms, coordinates and B's for the 10 H atoms, a scale factor and a secondary extinction parameter, g (Larson, 1967, equation 3; Zachariasen, 1963). The final results were $R = 0{\cdot}040$ and $R_w = 0{\cdot}045$ for 2531 reflexions.* The goodness-of-fit, defined as $[\sum w(|F_o| - |F_c|)^2/(m-s)]^{1/2}$, where m is the number of observations and s the number of parameters, was 1·90 and the secondary extinction coefficient, g, assumed the final value of $35{\cdot}8\ (2{\cdot}8) \times 10^{-6}$. Form factors for C and O were from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). The final atomic parameters are given in Table 1; the molecular geometry is reported in Fig. 1 and in Tables 2 and 3.

Table 3. *Bond angles* (°)

C(1)–C(2)–C(3)	124·6 (1)	C(5)–C(6)–C(15)	112·2 (1)
C(4)–C(5)–C(6)	125·1 (1)	C(9)–C(8)–C(16)	112·9 (1)
C(8)–C(9)–C(10)	125·2 (1)	C(12)–C(13)–C(16)	113·1 (1)
C(11)–C(12)–C(13)	124·7 (1)	C(2)–C(1)–C(15)	112·0 (1)
C(2)–C(3)–C(4)	129·0 (1)	C(7)–C(6)–C(15)	121·1 (1)
C(3)–C(4)–C(5)	129·8 (1)	C(7)–C(8)–C(16)	120·9 (1)
C(9)–C(10)–C(11)	129·6 (1)	C(16)–C(13)–C(14)	120·1 (1)
C(10)–C(11)–C(12)	129·0 (1)	C(15)–C(1)–C(14)	121·2 (1)
C(5)–C(6)–C(7)	126·1 (1)	C(6)–C(15)–O(1)	123·8 (1)
C(7)–C(8)–C(9)	125·5 (1)	C(1)–C(15)–O(1)	123·4 (1)
C(12)–C(13)–C(14)	126·5 (1)	C(8)–C(16)–O(2)	124·0 (1)
C(14)–C(1)–C(2)	126·4 (1)	C(13)–C(16)–O(2)	123·4 (1)
C(6)–C(7)–C(8)	122·7 (1)	C(1)–C(15)–C(6)	112·4 (1)
C(13)–C(14)–C(1)	123·3 (1)	C(8)–C(16)–C(13)	112·4 (1)
C(1)–C(2)–H(2)	115·3 (9)	C(8)–C(9)–H(9)	117·3 (7)
C(3)–C(2)–H(2)	119·9 (9)	C(10)–C(9)–H(9)	117·4 (8)
C(2)–C(3)–H(3)	116·9 (9)	C(9)–C(10)–H(10)	115·4 (8)
C(4)–C(3)–H(3)	113·2 (9)	C(11)–C(10)–H(10)	114·2 (8)
C(3)–C(4)–H(4)	115·3 (9)	C(10)–C(11)–H(11)	115·3 (9)
C(5)–C(4)–H(4)	114·4 (9)	C(12)–C(11)–H(11)	115·1 (9)
C(4)–C(5)–H(5)	119·3 (8)	C(11)–C(12)–H(12)	119·8 (8)
C(6)–C(5)–H(5)	115·6 (8)	C(13)–C(12)–H(12)	115·5 (8)
C(6)–C(7)–H(7)	118·4 (7)	C(13)–C(14)–H(14)	118·4 (7)
C(8)–C(7)–H(7)	117·4 (7)	C(1)–C(14)–H(14)	117·5 (7)

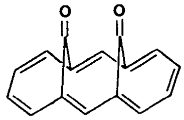
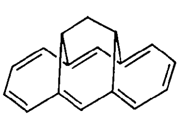
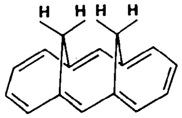
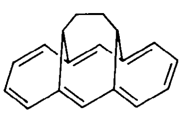
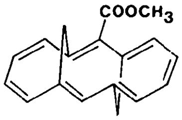
Discussion. The essential features of the annulene perimeter of BCA, that is (i) the approximate *mm*2 symmetry, (ii) the systematic changes of the bond lengths and (iii) the torsional angles along the annulene perimeter, are similar to those found in analogous compounds, *e.g.* SBM {*syn*-1,6:8,13-bismethano[14]-annulene (Destro, Pilati & Simonetta, 1977)}, BUT {1,6:8,13-butane-1,4-diylidene[14]annulene (Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1972)} and PAN {1,6:8,13-propane-1,3-diylidene[14]annulene (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972)}. Structural formulae for these compounds are given in Table 4.

For each of the four molecules we have evaluated the quantities $\bar{r} = \langle r_i \rangle$, $\rho = \langle (r_i - \bar{r})^2 \rangle^{1/2}$, $\tau = \langle \tau_i^2 \rangle^{1/2}$ and $D = \langle d_i^2 \rangle^{1/2}$, where r_i are the observed bond lengths in the ring, τ_i the torsion angles in the annulene perimeter and d_i the distances of each atom from the least-squares plane through all the atoms in the perimeter. The values are reported in Table 4, together with those calculated for the cyclopolyolefin ANTI {7-methoxycarbonyl-*anti*-1,6:8,13-bismethano[14]annulene (Gramaccioli, Mimun, Mugnoli & Simonetta, 1973)}. In agreement with the trend shown by slightly different quantities used by Gavezzotti & Simonetta (1976) in their extensive study on bridged annulenes, D should be rejected as a criterion of aromaticity, while both ρ and τ seem to be more adequate.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32757 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Comparison between geometrical parameters of the annulene ring in related compounds*

	BCA	PAN	SBM	BUT	ANTI
Compound					
r (Å)	1·396	1·394	1·393	1·397	1·404
ρ (Å)	0·013	0·012	0·017	0·024	0·060
τ (°)	20·7	20·5	23·4	24·8	34·0
D (Å)	0·31	0·28	0·43	0·43	0·30

The values of Table 4 could erroneously suggest that the annulene-ring conformations of BCA and PAN are virtually coincident. Actually, comparison of the *mm*2-averaged geometric parameters of the two molecules shows that the corresponding bond distances along the perimeters are effectively in close agreement, no difference being greater than the pooled e.s.d., while two torsion angles, C(1)–C(2)–C(3)–C(4) and C(13)–C(14)–C(1)–C(2), differ significantly (~4°). This is mainly due to the different strain imposed on the rings by the bridging groups, as could be argued by the values of the intramolecular C(15)···C(16) distance: 2·591 Å in BCA *vs* 2·434 Å in PAN. Furthermore, the different values of the bridge CCC angle (112·4° in the former and 104·2° in the latter molecule) imply a larger value for the C(1)···C(6) transannular distance in BCA (2·470 Å) than in PAN (2·359 Å).

Repulsive interactions between the two carbonyl groups give rise to significant bending of the O atoms out of the planes of their respective bridge C atoms, both deviations occurring in a direction away from the centre of the annulene ring. The different amounts of displacement [0·132 Å for O(1) and 0·086 Å for O(2)] can probably be ascribed to different packing interactions involving the two O atoms. As a result, the O(1)···O(2) distance is 3·014 Å.

The shortest intermolecular contacts between heavy atoms involve molecules related to one another by a centre of symmetry. They are: C(14)···C′(14), 3·255 Å, and C(14)···C′(13), 3·323 Å.

The anisotropic temperature factors of the heavy atoms were examined by the rigid-body treatment of Schomaker & Trueblood (1968). When all 18 atoms were included, the fit to a rigid-body model was unsatisfactory. Deletion of the four atoms of the carbonyl groups led to a considerably improved but not entirely satisfactory fit, many of the individual values of ΔU_{ij} being greater than three times their standard deviations. The lengths of principal axes of the **L** tensor were 22, 11 and 5 $(^\circ)^2$, and implied corrections to the interatomic distances in the range 0·004–0·007 Å.

We thank Professor E. Vogel for supplying crystals of the substance.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Destro, R., Pilati, T. & Simonetta, M. (1977). *Acta Cryst.* B**33**, 940–942.

Gavezzotti, A., Mugnoli, A., Raimondi, M. & Simonetta, M. (1972). *J. Chem. Soc. Perkin* II, pp. 425–431.

Gavezzotti, A. & Simonetta, M. (1976). *Helv. Chim. Acta*, **59**, 2984–2998.

Gramaccioli, C. M., Mimun, A. S., Mugnoli, A. & Simonetta, M. (1973). *J. Amer. Chem. Soc.* **95**, 3149–3154.

Gramaccioli, C. M., Mugnoli, A., Pilati, T., Raimondi, M. & Simonetta, M. (1972). *Acta Cryst.* B**28**, 2365–2370.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Vogel, E. & Balci, M. (1976). Personal communication.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.