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An aromatic hydrocarbon π-system with a 42° dihedral twist: X-ray crystal structure of 1,3-bis(trichloroacetyl)homoazulene

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Dedicated to Professor Dr Henning Hopf on the occasion of his 60th birthday

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Abstract—Red crystals of 1,3-bis(trichloroacetyl)homoazulene (**2**), prepared by Friedel–Crafts acylation of homoazulene (**1**), have been examined by X-ray diffraction. The 10 carbon–carbon bonds that make up the perimeter π-system of **2** average 1.402 Å in length, with an average deviation (absolute value) from this length of only 0.016 Å. Thus, like benzene, this nonbenzenoid π-system exhibits bond length convergence and thereby qualifies as 'aromatic' by the geometric criterion. The aromaticity of homoazulene (**1**) had previously been based on its magnetic, thermodynamic and chemical properties. The crystal structure of **2** also reveals that the 1,5-bridge severely distorts the [10]annulene π-system away from planarity and induces torsional angles as large as 42.2° at a bridgehead position. To the best of our knowledge, dihedral angles this large have never before been observed in any other π-system that is still capable of supporting cyclic delocalization of electrons. The 'homoconjugation' gap between the two bridgehead positions was found to be 2.254(5) Å. © 2001 Elsevier Science Ltd. All rights reserved.

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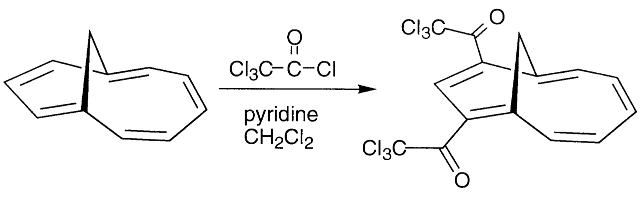
1. Introduction

Homoazulene (**1**)[1] is a nonbenzenoid aromatic hydrocarbon that satisfies all the criteria for 'aromaticity' against which it has been tested.[2] Like benzene, this bridged [10]annulene supports an induced diamagnetic ring current when placed in a strong, external magnetic field, and this behavior qualifies the compound as 'aromatic' by the magnetic criterion. Thus, in the ^{1}H NMR spectrum of **1**,[1b] the hydrogens projecting out from the perimeter are strongly deshielded and resonate at abnormally low field (δ 6.88–8.11 ppm, i.e. in the 'aromatic' region), whereas those on the methylene bridge are strongly shielded and resonate at abnormally high field (δ −0.67 to −1.18). Homoazulene also satisfies the thermodynamic criterion for aromaticity; heats of hydrogenation measurements[3] reveal that the parent hydrocarbon enjoys an 'aromatic stabilization' that is ca 25% of that measured for benzene, the benchmark for all aromatic compounds. Even the chemistry of homoazulene (e.g. Eq. (1))[4] resembles that of benzene; a tendency toward preservation of cyclic conjugation in the π-system favors electrophilic aromatic substitution in both cases.



1 **2**

(1)

We are now pleased to report that homoazulene, in addition to fulfilling the magnetic, thermodynamic and chemical criteria for aromaticity, also satisfies the geometric criterion for aromaticity, i.e. its π-system displays bond length convergence, as opposed to bond alternation. In benzene, the carbon–carbon bonds around the rim of the molecule are all intermediate in length between those of normal sp^2–sp^2 double bonds and normal sp^2–sp^2 single bonds, and the same is true for the crystalline homoazulene derivative (**2**) that we have examined by X-ray crystallography.

In addition to establishing the bond length convergence in this conjugated cycle, the X-ray crystallographic analysis reported here provides a quantitative assessment of the degree to which the homoazulene π-system is twisted out of planarity. A dihedral angle in the π-system of 42.2° is

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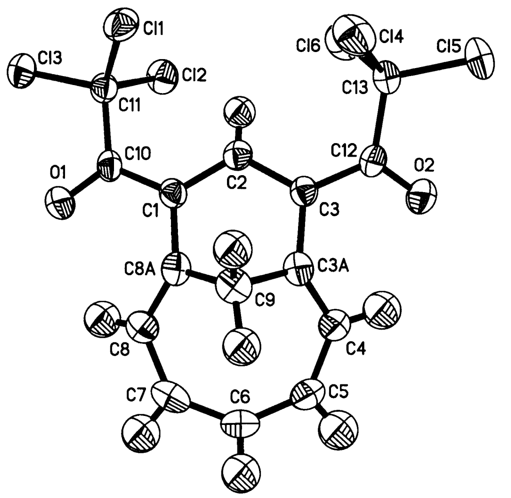


Figure 1. A view of **2** showing atomic numbering. The homoazulene ring system has been numbered according to traditional azulene numbering, rather than by the IUPAC convention. Ellipsoids enclose 30% probability.

seen at one of the bridgehead positions. To the best of our knowledge, dihedral angles this large have never before been observed in any other π-system that is still capable of supporting cyclic delocalization of electrons.

2. Results

Fig. 1 shows a view of the X-ray structure of **2** with atomic numbering. We have used traditional azulene numbering, rather than the IUPAC convention. A side view of the homoazulene core appears in Fig. 2, and the interatomic distances, angles and torsion angles for the core are listed in Table 1. As Fig. 2 reveals, the ten-membered ring is not planar, but eight of the atoms lie nearly in a plane, with the bridgehead atoms pulled out of the plane by the bridging methylene group. Atoms C1, C2, C3, C4, C5, C6, C7 and C8 are coplanar within ±0.041 Å (rms deviation 0.054 Å). The bridgehead atoms C3A and C8A lie above the plane by 0.446(4) and 0.390(4) Å, respectively, and the substituent atoms C10 and C12 lie below it by 0.580(5) and 0.266(5) Å, respectively. The degree of planarity may also be estimated from the perimeter torsion angles in Table 1. The absolute values $|\tau|$ range from 4.9 to 26.2° for the angles about the bonds in the plane, whereas the torsion angles at the bridgehead atoms are all larger, ranging from 27.1 to 42.2° ($|\tau|=180-|\tau|$ for $|\tau|>90°$).

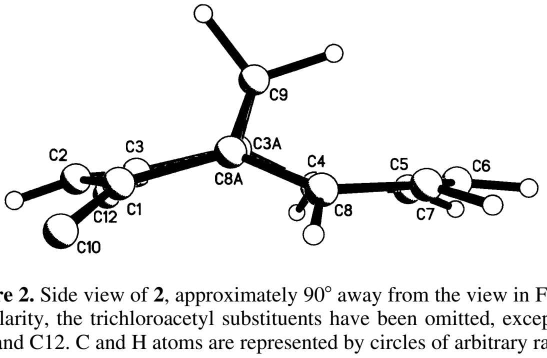


Figure 2. Side view of **2**, approximately 90° away from the view in Fig. 1. For clarity, the trichloroacetyl substituents have been omitted, except for C10 and C12. C and H atoms are represented by circles of arbitrary radius.

Eight of the bond distances around the perimeter of the homoazulene core are typical of aromatic compounds (1.378–1.404 Å), while the other two, C1–C8A (1.435 Å) and C3–C3A (1.448 Å), are significantly longer. The perimeter torsion angles $|\tau|$ about the long bonds (35.1 and 42.2°) are the largest of the four bridgehead values.

Hydrogen atom positions were located geometrically but then refined (with displacement parameters based on those of their attached C atoms) since the C–C–C bond angles at C5, C6, C7 and C8 are much larger than 120°, and that at C9 is much smaller than 109.5° (Table 1). All the perimeter H atoms except H6 lie on the side of the 8-peripheral-atom plane away from the bridge (Fig. 2).

That the two trichloroacetyl groups sit in different environments in the crystal can be seen in the anisotropic displacement parameters (see Fig. 1) and in the intermolecular contacts. Treatment of the molecule as a librating rigid body with two attached rigid trichloromethyl groups[5] leads to a torsional vibration amplitude of 3.5(7)° for Cl1, Cl2 and Cl3 about the C11–C10 axis and of 6.6(4)° for Cl4, Cl5 and Cl6 about the C13–C12 axis. This analysis increases C–C and C–O bond lengths by about 1 e.s.d., whereas C–Cl bond lengths increase by 2.5–3 e.s.d. for Cl1, Cl2 and Cl3, and by 4–5 e.s.d. for Cl4, Cl5 and Cl6.

The most important intermolecular contacts appear to be between chlorine atoms; Cl1, Cl2 and Cl3 approach a total of six neighboring Cl atoms at distances from 3.61 to 3.95 Å, while Cl4, Cl5 and Cl6 make four such contacts, 3.32 to 3.84 Å in length.

3. Discussion

In the crystal, the two trichloroacetyl groups of **2** are twisted to different degrees with respect to the homoazulene core (see Fig. 1) and this destroys the C_s symmetry expected for the parent hydrocarbon. Nevertheless, the 10 carbon–carbon bonds that make up the perimeter π-system of **2** average 1.402 Å in length (cf. benzene: 1.398 Å),[6] and, despite the two relatively long bridgehead bonds mentioned above, the average deviation (absolute value) from this length is only 0.016 Å. The average length of the bonds around the π-system of **2** thus falls almost exactly halfway between 1.345(12) and 1.455(11) Å values found, respectively, for the average lengths of the C=C and C–C seen in X-ray structures of conjugated aliphatic hydrocarbons.[7]

The bridgehead carbon atoms of **2** are separated by 2.254(5) Å, and this distance is not great enough to completely insulate one side of the π-system from the other. We have previously reported experimental evidence for a significant 'homoconjugative' interaction between the two bridgehead p-orbitals of homoazulene derivatives,[8] a property that justifies referring to this 1,5-methano[10]annulene as 'homoazulene.'

The absolute values of the dihedral angles defined by successive 4-atom segments in the perimeter π-system of **2** vary from 4.9(10) to 42.2(5)° (see Table 1). It is remarkable that electron delocalization is able to persist around a cyclic

Table 1. Selected distances, angles and torsion angles in **2**

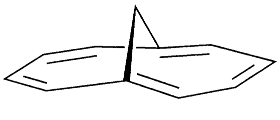
Atom 1	Atom 2	Atom 3	Atom 4	Distance (Å) 1–2	Angle (°) 1–2–3	Torsion angle τ (°) 1–2–3–4
C1	C2	C3	C3A	1.403(5)	121.3(3)	−13.1(5)^{a}
C2	C3	C3A	C4	1.402(5)	114.5(3)	137.8(4)^{a,b}
C3	C3A	C4	C5	1.448(5)	129.9(4)	−152.9(5)^{a,b}
C3A	C4	C5	C6	1.379(5)	124.3(4)	18.4(9)^{a}
C4	C5	C6	C7	1.391(6)	134.3(4)	12.2(11)^{a}
C5	C6	C7	C8	1.378(6)	135.1(4)	−4.9(10)^{a}
C6	C7	C8	C8A	1.397(7)	133.6(4)	−26.2(8)^{a}
C7	C8	C8A	C1	1.404(6)	123.2(4)	152.6(4)^{a,b}
C8	C8A	C1	C2	1.382(6)	131.0(4)	−144.9(4)^{a,b}
C8A	C1	C2	C3	1.435(5)	114.9(3)	15.8(5)^{a}
C7	C8	C8A	C9			−20.1(6)
C1	C8A	C9	C3A		113.2(4)	−67.1(4)
C8	C8A	C9	C3A		115.5(4)	106.8(4)
C8A	C9	C3A	C4	1.485(6)	98.5(3)	−102.4(4)
C9	C3A	C3	C12	1.489(5)	111.7(3)	152.8(3)
C9	C3A	C4	C5		117.9(4)	17.3(7)
C3A	C8A	C1	C2	2.254(5)	93.7(3)	−9.3(4)
C2	C3	C3A	C8A			4.8(4)
C3	C3A	C8A	C1		93.9(3)	2.6(3)
C10	C1	C8A	C8	1.459(5)	119.8(3)	28.8(6)
C12	C3	C3A	C4	1.452(5)	119.9(3)	−36.5(6)
O1	C10	C1	C2	1.209(4)	122.3(4)	170.2(4)
O2	C12	C3	C3A	1.200(4)	123.1(4)	20.2(6)
C11	C10	C1	C2	1.551(5)	121.1(3)	−10.0(5)
C13	C12	C3	C2	1.565(5)	120.2(3)	28.5(5)
Cl1	C11	C10	C1	1.765(4)	111.9(3)	−52.0(4)
Cl2	C11	C10	C1	1.780(4)	108.6(2)	69.3(4)
Cl3	C11	C10	C1	1.756(4)	110.6(2)	−172.7(3)
Cl6	C13	C12	C3	1.750(4)	111.5(3)	43.4(4)
Cl4	C13	C12	C3	1.763(4)	108.5(3)	−77.4(4)
Cl5	C13	C12	C3	1.752(4)	110.3(2)	164.6(3)

Redundant values omitted.

[a] Perimeter torsion angles in the π-system.

[b] Bridgehead torsion angles.

π-system that suffers from such severe twisting. Comparisons with the isomeric 1,6-methano[10]annulene (**3**) and with the *anti*-dimethano[14]annulene (**4**) are instructive.



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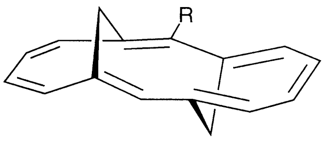

4

The largest dihedral angle in the perimeter π-system of **3** (35.6°)[9] is also seen at the bridgehead position, but the twisting is less severe than that present in **2**. This bridged [10]annulene, like homoazulene, also satisfies the magnetic, thermodynamic, chemical and geometric criteria for aromaticity.[3,10,11] Several substituted derivatives of **3** have somewhat more twisted π-systems than the parent hydrocarbon; however, all but one show less bond length convergence around the perimeter than either **2** or **3**, and none is as drastically twisted as **2**.[12]

In contrast to the situation in these bridged [10]annulenes, the largest dihedral twist in the perimeter π-system of **4** (75.1°, R=COOMe)[11,13] falls beyond what is necessary to break the cycle of conjugation. There is no detectable aromatic character associated with **4**.[13,14] The bonds alternate in length between short and long around the perimeter, and there is no ring current reflected in the ^{1}H NMR spectrum of the compound. Apparently, a dihedral twist of 75.1° causes too great a misalignment of p-orbitals to preserve any significant π-bonding.[15]

Our experimental results for **2** show that aromatic π-systems can tolerate dihedral twists in excess of 42° without losing their aromaticity. How much more dihedral twist an aromatic π-system can tolerate before the effects of cyclic conjugation are lost remains an open question.

4. Experimental

A sample of 1,3-bis(trichloroacetyl)homoazulene (**2**), prepared as indicated in Eq. (1),[4] was recrystallized from hexane to give dark red needles (mp 161–162°C) which proved on inspection to be bundles of thin plates. An apparently single plate was studied in 1988, with MoKα radiation. The crystals belong to the monoclinic system with β near 90°, and many pairs of reflections ($h\ k\ l$ and $h\ k\ -l$ or $h\ -k\ l$) were examined to verify crystal symmetry. The structure was solved by direct methods in space group $P2_1/n$, $Z=4$. The intensities at room temperature were weak, but data collected at low temperature, though more intense, gave indications that the crystal was not single or that the structure was disordered. Nevertheless, refinement was carried out to convergence. We now report the structure based on new data collected at room temperature on a very thin plate, about 0.001 mm thick, using a Bruker SMART 1K CCD.[16] The crystals had been stable over the

Table 2. Crystal data

	298 K, 1988	128 K, 1988	298 K, this work
a (Å)	5.943(3)	5.875(3)	5.9322(12)
b (Å)	14.767(8)	14.561(7)	14.751(3)
c (Å)	19.812(11)	19.652(9)	19.877(4)
β (°)	89.815(14)	90.041(12)	90.120(4)
V (Å^3)	1738.8(17)	1681.0(13)	1739.4(6)
Crystal size (mm^3)	0.05×0.26×0.36	0.05×0.26×0.36	0.001×0.30×0.45
$\theta_{\max}$(°)	22.55	32.49	28.29
Reflns (unique)	2287	4024	4151
Reflns ($I>2\sigma(I)$)	1028	1962	1891
Refined parameters	208	208	232
$R(F)$, ($I>2\sigma(I)$)	0.084	0.088	0.047
$wR(F^2)$	0.279	0.279	0.136
$\Delta\rho_{\max}$ (e Å^{-3})	0.33	0.67	0.34
$\Delta\rho_{\min}$ (e Å^{-3})	−0.42	−0.72	−0.27

intervening years, and the structure is essentially the same as that determined earlier. However, the precision of the analysis is much improved and there is no indication of disorder. Crystal data and refinement parameters for the three analyses are presented in Table 2. The Crystallographic Information File (CIF) has been deposited at the Cambridge Crystallographic Data Centre under the compound name 8,10-bis(trichloroacetyl)bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene (ID CCDC 153029).

Acknowledgements

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References

1. (a) Masamune, S.; Brooks, D. W.; Morio, K.; Sobczak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 8277–8279. (b) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239–3240. (c) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A. *Angew. Chem.* **1981**, *93*, 282–283. (d) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5216–5220.
2. For general discussions of criteria for aromaticity, see: (a) Lewis, D.; Peters, D. *Facts and Theories of Aromaticity*, Crane Russak: New York, 1975. (b) Garratt, P. J. *Aromaticity*, Wiley: New York, 1986. (c) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*, Wiley: New York, 1994.
3. Roth, W. R.; Boehm, M.; Lennartz, H. W.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1007–1008.
4. (a) Scott, L. T.; Sumpter, C. A.; Oda, M. *Tetrahedron Lett.* **1989**, *30*, 305–308. (b) Sumpter, C. A. MS Thesis, University of Nevada, Reno, 1989.
5. Schomaker, V.; Trueblood, K. N. *Acta Crystallogr. B* **1998**, *54*, 507–514.
6. Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; Pople, J. A. *Proc. R. Soc. Lond., Ser. A* **1987**, *414*, 47. For comments on the accuracy of this bond length in X-ray structures, see Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 782–784.
7. *International Tables for X-ray Crystallography*; Kluwer Academic: Dordrecht, 1992, vol. C, p 695.
8. (a) Scott, L. T.; Oda, M.; Erden, I. *J. Am. Chem. Soc.* **1985**, *107*, 7213–7214. (b) Scott, L. T.; Oda, M. *Tetrahedron Lett.* **1986**, *27*, 779–782. (c) Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 105–110.
9. Bianchi, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr. B* **1980**, *36*, 3146–3148.
10. (a) Vogel, E.; Roth, H. D. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 228–229. (b) Vogel, E. *Spec. Publ. Chem. Soc.* **1967**, 113–147.
11. Vogel, E. *Chimia* **1968**, *22*, 21–32.
12. (a) Dobler, M.; Dunitz, J. D. *Helv. Chim. Acta* **1965**, *48*, 1429–1440. (b) Bianchi, R.; Morosi, G.; Mugnoli, A.; Simonetta, M. *Acta Crystallogr. B* **1973**, *29*, 1196–1204. (c) Pilati, T.; Simonetta, M. *Acta Crystallogr. B* **1976**, *32*, 1912–1913. (d) Meyer, A.; Schlögl, K.; Pertlik, F. *Monatsh. Chem.* **1990**, *121*, 1045–1051.
13. (a) Gramaccioli, C. M.; Mimun, A. S.; Mugnoli, A.; Simonetta, M. *Chem. Commun.* **1971**, 796. (b) Gramaccioli, C. M.; Mimun, A. S.; Mugnoli, A.; Simonetta, M. *J. Am. Chem. Soc.* **1973**, *95*, 3149–3154. (c) Simonetta, M. *Pure Appl. Chem.* **1980**, *52*, 1597–1610.
14. Vogel, E.; Haberland, U.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 513–514.
15. (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137–142. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676–1685.
16. Bruker SAINT 6.02, Bruker AXS, Madison, WI, 1999.