Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 45 (2004) 2167–2170

Tetrahedron Letters

The cyclopropa[*b*]naphthalene electron donor: nonplanar 8π 7C cycloheptatrienylidene derivatives☆

Brian Halton,[a,*] Roland Boese[b,*] and Gareth M. Dixon[a]

[a]*School of Chemical and Physical Sciences, Victoria University, PO Box 600, Wellington, New Zealand*
[b]*Institute for Inorganic Chemistry, University of Essen, Universitaetsstr. 3-5, 45117 Essen, Germany*

Received 28 November 2003; revised 22 December 2003; accepted 9 January 2004

Abstract—Dipole moment measurements and calculations show the cyclopropa[*b*]naphthalene moiety to be an electron donor that is stronger than cycloheptatriene. Crystallographic analyses of cycloheptatrienylidenecyclopropa[*b*]naphthalenes, with and without electron donating substituents in the cycloproparene, have the seven-membered ring resisting imposition of 8π 7C antiaromaticity by bending significantly out of the plane that carries the cycloproparene. The extent of this distortion depends upon the level of electron donation from the cycloproparene.

The class of strained aromatic hydrocarbons known as the cycloproparenes, and illustrated by parent **1**, has provided much fascinating chemistry[1] since the report of the first authenticated derivative in 1964.[2] The fact[3] that the pK_a of **1** is ca. 36 means that C1 cyclopropabenzenyl and cyclopropa[*b*]naphthalenyl anions are easily available for use in synthesis. This has been applied especially in Peterson olefinations[4] to give alkenes, for example, **2**, for which many fundamental facets remain to be explored. We present here the results of synthetic, physical and structural studies that (i) confirm that the cyclopropa[*b*]naphthalenylidene moiety is an electron donor, (ii) show by X-ray analyses that the cycloheptatriene moiety of the derived fulvalenes **19–21** is bent significantly from planarity, and (iii) demonstrate that this bending increases with increasing electron donation from the cycloproparene. We take the results as a measure of resistance to the development of 8π 7C antiaromaticity in the conjugated seven-membered ring.

Some time ago it was shown that the cycloproparenyl moiety of fulvenes[5] **2** can sustain both positive and negative charge. Thus, the measured dipole moments of the fluorenylidene derivatives **4** and **5**, with a cyclopentadienyl electron sink,[6,7] and the *p*,*p*′-bis(dimethylaminophenyl) congeners **6** and **7**, with strong mesomeric donors in the alkene substituents (Table 1), were presumed to lie in opposite directions.[8] The marked polarity recorded earlier[8] for **7** and that measured here for the known[9] *p*,*p*′-bis(dinitrophenyl) analogue **8** (Table 1) are analogous. Calculations (HF/6-31G**) now show the dipoles of **4**, **5** and **8** to lie towards the electron acceptors (giving cycloproparenyl cation character) while those of **6** and **7** lie in the opposite direction (generating electron-rich cycloproparenes) as intuitively expected. In this regard it must be noted that the direction of a dipole and its relative order among a group of closely related molecules is reliably calculated by simple ab initio methods. However, for a reasonable estimate of the dipole magnitude higher-level calculations must be performed, for example, at the HF/6-31G(d,p) level.[6,7]

Methylidenecyclopropabenzene **2** ($R^1 = R^2 = H$) is not known,[1] but it is expected[6] to be *less* strained than **1** by ca. 2 kcal mol^{-1} and to have a dipole moment of 1.8 D (from HF/6-31G(d,p) calculations) that is directed towards the exocyclic CH_2 centre (see Chart 1). This dipole lies in the *same* direction as that calculated for parent heptafulvene **3** ($R^1 = R^2 = H$), but its magnitude is markedly higher. The dipole moment of **3** ($R^1 = R^2 = H$) was determined from microwave studies as 0.48 D and is computed as 0.27 D.[10] The measured polarities of the simple diphenyl-substituted

---

Keywords: Antiaromaticity; Strained molecules; Fulvalenes; Dipole moments; Crystal structures.

☆ Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tetlet.2004.01.031

* Corresponding authors. Tel.: +64-44635954; fax: +64-4465241; e-mail: brian.halton@vuw.ac.nz

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.01.031

Table 1. Measured and calculated dipole moments of alkylidenecycloproparenes **4**–**15** and **19**–**23**

Compound	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**19**	**20**	**21**	**22**	**23**
μ (D)	2.6	3.3	2.2	3.0	4.3	1.0	0.4(2)	1.2	2.3	2.6[a]	4.3[a]	1.7[a]	1.2	1.6	1.8(5)	1.4(5)	1.6
Reference	6,7	6,7	8	8	[b]	7	7[b]	[b]	[b]	6	6	6	7[b]	[b]	[b]	[b]	[b]

[a] Calculated value.

[b] This work; experimental details are provided in the supplementary material.

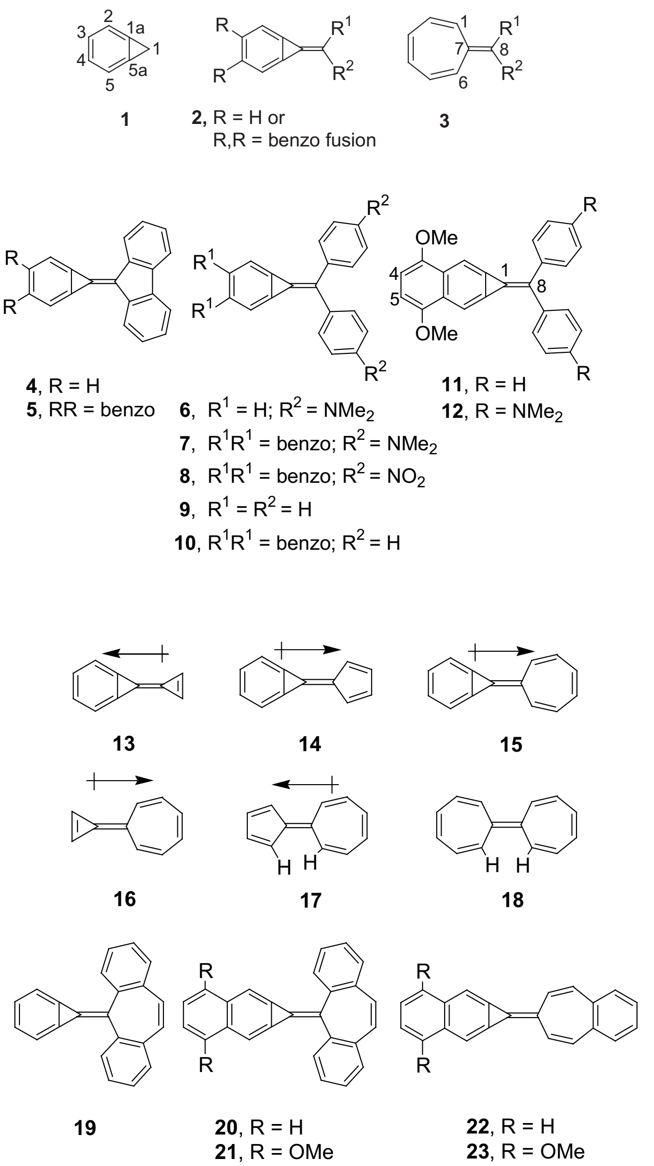

Chart 1.

cycloproparenes **9** and **10** (Table 1)[7] are also higher than that calculated ($\mu = 0.11$ D)[10b] for the known[11] **3** ($R^1 = R^2 = Ph$) but all three have the polarity directed towards the exocyclic centre.[10b] When coupled with δ_C/σ_p^+ correlations for *p*- and *p,p′*-di-substituted 1- and 1,1-diarylmethylidenecycloproparenes,[12] the measured dipoles imply the cycloproparenyl moiety to be an electron donor.

We now find the measured dipole of the electron donating cyclopropa[*b*]naphthalene-3,6-diether[13] **11** to be *higher* than its nonether parent[7] **10** by 0.8 D, viz. the electron donating ether substituents in the cycloproparenyl moiety reinforce the dipole. Furthermore, the analogous *p,p′*-diaminodiether **12** has a dipole moment that is 0.7 D *lower* than that of the diamino nonether[8] **7** (Table 1) showing that the remote electron donating groups oppose the dipole from the cycloproparene. These unambiguous new results for the exocyclic diaryl derivatives confirm that the cyclopropa[*b*]naphthalene moiety is a weak donor, improved by the presence of suitably located electron donating substituents within the ring system. Furthermore, they imply it to be a better donor than a cycloheptatrienyl unit.

When a conjugated ring is fused to C1 of a cycloproparene a novel polar fulvalene hydrocarbon is formed. Earlier calculations have shown[6] that it is only the as yet unknown cyclopropenylidene derivative **13** that has its dipole moment (2.6 D; Table 1) directed towards the cycloproparene. The unknown cyclopentadienylidene **14** and cycloheptatrienylidene **15** derivatives are both predicted as polar (Table 1), but with the dipole directed *away* from the cycloproparene and *towards* the fused ring (Chart 1). The expectation, calculation and observation[6] of a polar cyclopentadienylidene electron sink in **4** and **5** are unexceptional. The prediction of a cyclopropenyl cation in **13** is untested though not too surprising.[14] The calculation of a dipole directed *towards* the traditional electron donating cycloheptatrienylidene moiety of **15**, formally to liberate an 8π 7C antiaromatic cycloheptatrienyl anion, is at first sight unexpected. It is fully compatible, however, with the results provided above that imply the cycloproparenyl moiety to be a stronger electron donor than a cycloheptatriene. Furthermore, calculations show a strong dipole [3.76 D,[14b] HF/6-311G(3d,2p); 3.64 D,[10b] HF/6-31G**] directed towards the seven-membered ring of unknown triaheptafulvalene **16**.

Structural studies have shown that parent heptafulvene **3** ($R^1 = R^2 = H$) is planar[15] but that 8,8-disubstituted derivatives are bent out of plane.[5] Pentaheptfulvalene **17** and bicycloheptatrienylidene **18** are also distorted from planarity[14] because of nonbonded interactions between the proximal H2 and H2′ atoms (Chart 1), the former to only a slight extent. Triaheptafulvalene **16** is predicted to be planar but is unknown[14] and there is only one recorded derivative that carries electron donors in the three-membered ring of the hydrocarbon in the absence of a tropone as the seven-membered ring, namely the 1,2-bis(di-isopropylamino) derivative; it was prepared in solution and spectral data only are available.[16] The concept of electron rich cycloheptatrienes is not new, especially when the seven-membered ring carries the recognised electron donors and Daub[17] has pointed out that such molecules prefer bond localisation and nonplanarity.

While the parent hydrocarbon **15**, formed from conjugation of cyclopropabenzene with cycloheptatriene, is not known, the dibenzo derivatives **19** and **20** were prepared some years ago using suberone.[6] The dipole moment of **19** is confirmed[7] from re-determination as 1.2 D while that of **20** is 1.6 D (Table 1). The dipole moment of **19** is smaller than that of naphthalene analogue **20** and, in turn, this is lower than that now reported for the previously prepared[13] diether **21** (1.85 D, Table 1). The trend to a more polar diether (as recorded also for **10** and **11** above) is mirrored also by the benzo[*c*] analogues **22**[7] and **23**. That diethers **21** and **23** are each *more* polar than their nonether counterpart shows that in the heptafulvalenes **20**–**23** the dipole moment is directed *from* the cycloproparene *to* the seven-membered ring as occurs for the phenyl derivatives **9**–**11**.

To assess the impact of electron donation on the structure of the cycloheptatrienylidene derivatives, crystallographic analyses have been carried out. The X-ray crystal structure[6] of cyclopropabenzene **19** shows the molecule to be markedly distorted from planarity with the cycloheptatrienylidene –CH=CH– unit bent out from the plane containing the cycloproparene by ca. 28°. The somewhat more polar naphthalene homologue **20** has not provided suitable crystals for analysis, but the even more polar naphtho diether **21** has.[18] An ORTEP plot of **21** at 30% probability is given in Figure 1 with selected bond lengths and angles appended. Distortion of the seven-membered ring from planarity is shown by the side view of Figure 2, while Figure 3 shows the superimposition of the structure of benzononether **19** on that of naphtho diether **21**. The effect of this is to show that there is markedly more distortion (by some 17°) of the cycloheptatrienylidene moiety from the cycloproparene plane in the more polar **21** (to ca. 45°) than occurs in **19**. The $H2\cdots H2'$ nonbonded interactions that are a feature of **17** and **18** cannot be present in **15** since the cycloproparenyl moiety has no such *ortho* hydrogens as it is, itself, a 2,7-didehydrocycloheptatriene. However, the proximal *ortho* hydrogens of the suberone-derived moiety could interact with a lateral σ bond of the fused cyclopropene ring in **19**–**21** causing some distortion. Calculations at the HF/6-31G** level give separations to mid-C1–C1a of ca. 2.81 Å in the equilibrium geometry of each of **19**–**21**. In contrast, those for the $H2\cdots H2'$ distances in **17** and **18** (*transoid*/*cisoid*) are markedly less at ca. 2.13, and 2.38/2.11 Å, respectively. The recorded bendings of the cycloheptatrienylidene ring in the cycloproparenes **19** and **21** (and presumed for **20**) are interpreted appropriately, therefore, as a physical resistance in the conjugated seven-membered ring to the development of 8π 7C antiaromatic character that would otherwise be enforced by the stronger electron donating cycloproparene. That the distortion is greater in the more polar diether **21** than nonether **19** adds further credence to this. By way of contrast, the fluorenylidene derivatives **4** and **5** that carry a 6π 5C aromatic cyclopentadienylidene electron sink and an aromatic cycloproparenylidene cation are held essentially planar throughout.[6]

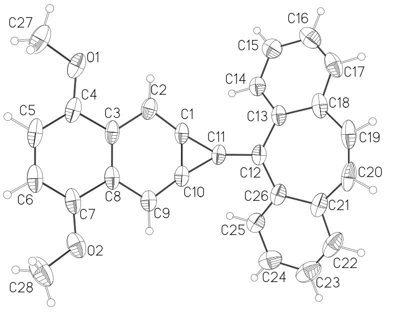

Figure 1. Perspective thermal ellipsoid plot (30%) of **21** (crystallographic numbering) viewed on the naphthalene rings. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.350(4); C(1)–C(10) 1.358(4); C(1)–C(11) 1.422(4); C(2)–C(3) 1.427(4); C(11)–C(12) 1.356(4); C(2)–C(1)–C(10) 124.6(3); C(1)–C(2)–C(3) 113.8(3); C(2)–C(3)–C(8) 121.7(2); C(1)–C(10)–C(11) 61.5(2); C(1)–C(11)–C(10) 56.98(19); C(12)–C(11)–C(1) 151.5(3).

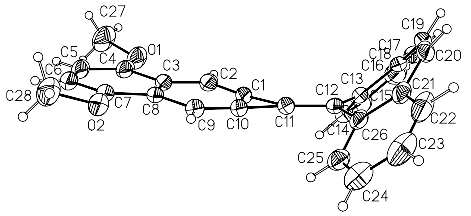

Figure 2. Perspective thermal ellipsoid plot (30%) of diether **21** (side view). Selected interplanar angles: *p*(C1,C10)/*p*(C1,C10,C11) 4.0°; *p*(C1,C10, C11)/*p*(C12,C13,C26) 3.1°; *p*(C12,C13,C26)/*p*(C13,C18,C21,C26) 39.5°; *p*(C13,C18,C21,C26)/*p*(C18,C19,C20,C21) 17.0°; *p*(C12,C13, C18,C19)/*p*(C13–C18) 4.1°; *p*(C12,C20,C21,C26)/*p*(C21,C26) 2.9°.

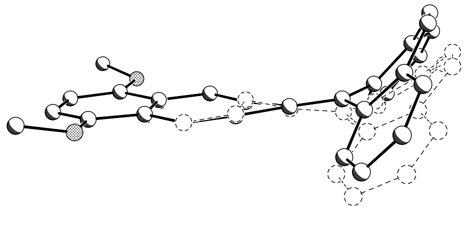

Figure 3. Superimposed side perspectives of cycloheptatrienylidenes **21** (solid lines) and **19** (broken lines).

It is unusual for the crystal structure of a fulvalene to reveal major bond length and angle differences from the independent ring systems of its makeup and this is true here also. The significance of the present results lies with the increase in distortion from **19** to **21** reflecting the increase in electron donation towards the cycloheptatriene unit of these novel heptafulvenes.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Victoria University for support.

References and notes

1. Halton, B. *Chem. Rev.* **2003**, *103*, 1327–1370; Halton, B. *Chem. Rev.* **1989**, *89*, 1161–1185.
2. Anet, R.; Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 525–526.
3. Eaborn, C.; Eidenschink, R. S.; Harris, J.; Walton, D. R. M. *J. Organomet. Chem.* **1977**, *124*, C27–C29; Eaborn, C.; Stamper, J. G. *J. Organomet. Chem.* **1980**, *192*, 155–161.
4. Halton, B.; Dixon, G. M. *Org. Lett.* **2002**, *4*, 4563–4565; Halton, B.; Cooney, M. J.; Boese, R.; Maulitz, A. H. *J. Org. Chem.* **1998**, *63*, 1583–1590; Halton, B.; Stang, P. J. *Synlett* **1997**, 145–158.
5. For fulvene review see: Neuenschwander, M. In *The Chemistry of the Double Bond Functional Group*; Patai, S., Ed.; Wiley Interscience: Chichester, 1989; Vol. 2, Suppl. A, Pt. 2, pp 1131–1268.
6. Apeloig, Y.; Boese, R.; Bläser, D.; Halton, B.; Maulitz, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 10147–10153.
7. Halton, B.; Buckland, S. J.; Lu, Q.; Mei, Q.; Stang, P. J. *J. Org. Chem.* **1988**, *53*, 2418–2422.
8. Halton, B.; Lu, Q.; Stang, P. J. *J. Chem. Soc., Chem. Commun.* **1988**, 879–880.
9. Halton, B.; Lu, Q.; Stang, P. J. *Aust. J. Chem.* **1990**, *43*, 1277–1282.
10. (a) Bauder, A.; Keller, C.; Neuenschwander, M. *J. Mol. Spectrosc.* **1976**, *63*, 281–287; (b) This work—calculated at the HF/6-31G** level.
11. Komatsu, K.; Fujimori, M.; Okamoto, K. *Tetrahedron* **1977**, *33*, 2791–2797.
12. Halton, B.; Lu, Q.; Stang, P. J. *J. Org. Chem.* **1990**, *55*, 3056–3060; Halton, B. *Pure Appl. Chem.* **1990**, *62*, 541–546.
13. Halton, B.; Kay, A. J.; Zhi-mei, Z.; Boese, R.; Haumann, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1445–1452.
14. (a) Scott, A. P.; Agranat, I.; Biedermann, P.; Riggs, A. P.; Radom, L. *J. Org. Chem.* **1997**, *62*, 2026–2038; (b) Hinchliffe, A. M.; Humberto, J. S. *Int. J. Mol. Sci.* **2000**, *1*, 39–48, online computer file. Available from: http://www.mdpi.org/ijms/papers/i1030039.pdf.
15. Bauer, W.; Laube, T.; Seebach, D. *Chem. Ber.* **1985**, *118*, 764–773.
16. Yoshida, Z. *Pure Appl. Chem.* **1982**, *54*, 1059–1074.
17. Daub, J.; Jenneskens, L. W. *Chimia* **1987**, *41*, 52–59; Daub, J.; Hirmer, G.; Jakob, L.; Maas, G.; Pickl, W.; Pirzer, E.; Rapp, K. M. *Chem. Ber.* **1985**, *118*, 1836–1856.
18. Crystal structure determination of **21**: $C_{28}H_{20}O_2$ *1/2C_5H_{12}, colourless crystal, dimensions $0.28 \times 0.26 \times 0.11$ mm, measured on a Siemens SMART-CCD diffractometer with Mo K_α-radiation. $T = 203(2)$ K. Cell dimensions $a = 10.734(5)$, $b = 26.067(13)$, $c = 7.870(5)$ Å, $\beta = 102.86(2)°$, $V = 2146.8(19)$ Å^3, monoclinic crystal system, $Z = 4$, $d_{\text{calcd}} = 1.313\,\text{g cm}^{-3}$, $\mu = 0.080\,\text{mm}^{-1}$, space group $P2_1/c$, data collection of 14,548 intensities, 5222 independent ($R_{\text{merg}} = 0.0341$, $\Theta = 2.33$–$25.08°$), 2460 observed [$F_o \geqslant 4\sigma(F)$], absorption correction with Siemens SADABS programme: R_{merg} before/after: 0.0632/0.0286, max/min transmission 1.00/0.19; structure solution with direct methods (SHELXS) and refinement on F^2 (SHELXTL 5.03) (287 parameters), the hydrogen atom positions were calculated and refined as riding groups with the 1.2-fold (1.5-fold for the methyl group) of the corresponding C-atoms. $R1 = 0.0797$, $wR2$ (all data) $= 0.2336$, $w^{-1} = \sigma^2(F_o^2) + (0.01531 \cdot P)^2 + 0.244 \cdot P$, where $P = [\max F_o^2) + (2F_c^2)]/3$, maximum residual electron density $0.529\,\text{e}\,\text{Å}^{-3}$. Pentane carbon atoms C(29)–C(32) were refined isotropically and disordered over two sites with occupancies 0.5 together with the riding hydrogen atoms. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 217077. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk) or from www.ccdc.cam.ac.uk/conts/retrieving.html