8-(Heptafulven-8-yl)-*p*-tropoquinone Methide

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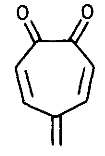
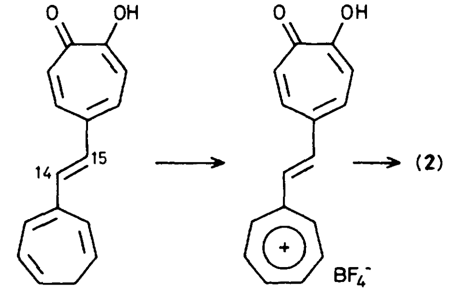
A novel *p*-tropoquinone methide-type compound has been synthesized; it has a high electron affinity and the molecule rotates about the exocyclic methylene double bond with a very low energy barrier in preference to the intercyclic single bond.

Despite the long history of troponoid chemistry, little is known so far about tropoquinone methide (**1**)-type compounds, seven-membered ring analogues of *p*-benzoquinone methide. Reports of such compounds are restricted to heptatriafulvalene-3,4-diones[1] and heptafulvalene-3,4-dione[2] carrying a conjugated three- and seven-membered π-ring respectively, instead of the exocyclic methylene group of (**1**). Considering the increasing interest in non-benzenoid quinonoid compounds in connection with new types of redox systems, new materials for optoelectronics, and antibiotic activity, we have now synthesized the title compound (**2**), the first of a series of *p*-tropoquinone methide (**1**)-type derivatives and have characterized its unique properties in relation to the electronic structural features of the unknown (**1**).

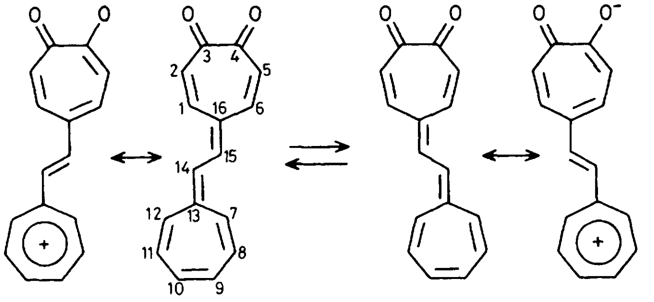
Wittig reaction of lithium 5-formyltropolonate with cyclohepta-1,3,6-trienylmethylenetriphenylphosphorane[3] in



(**1**)



(**3**) (**4**)



(**2a**) (**2**) (**2′**) (**2′a**)

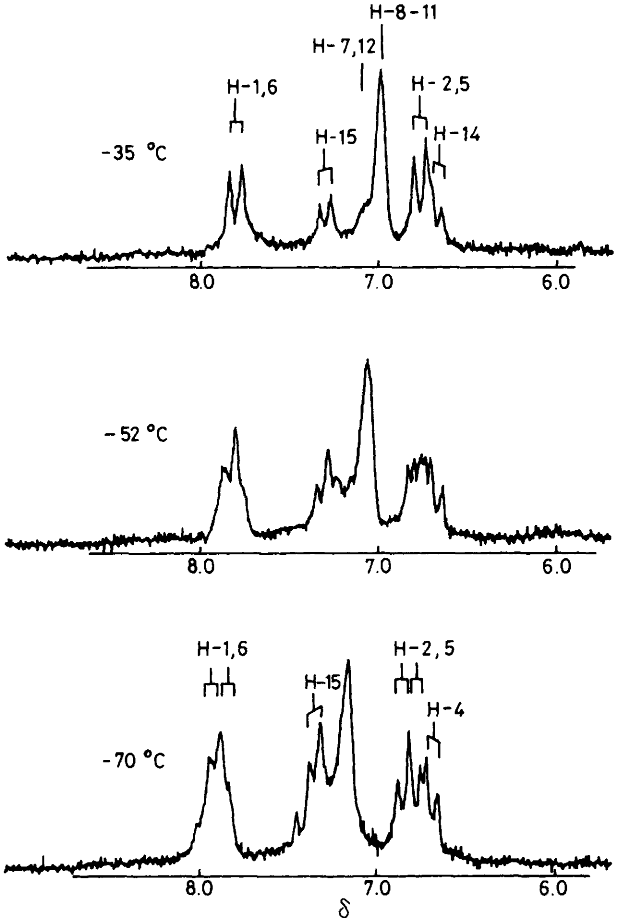


Figure 1. ^{1}H N.m.r. spectra (200 MHz; CD_2Cl_2) of the *p*-tropoquinone methide (**2**) at different temperatures.

tetrahydrofuran (THF) at −20 °C for 30 min afforded the key starting compound (**3**)† in 60% yield, hydride abstraction from which with trityl fluoroborate in dichloromethane at 0 °C gave the stable cation (**4**)‡ in 70% yield. The s-*trans* (*E*) conformations of (**3**) and (**4**) are indicated by the values of their ^{1}H n.m.r. vicinal coupling constants $J_{14,15}$. On treatment with an equimolar amount of triethylamine in dichloromethane at −78 °C under argon, (**4**) yielded quantitatively and reversibly a deep blue solution of (**2**) (2.56×10^{-2} mol/l), the presence of which was shown by 200 MHz ^{1}H n.m.r. analysis (Figure 1). The quinone methide (**2**) was gradually destroyed at room temperature within 30 min in dichloromethane solution of the above concentration and was not isolable in the solid state, whereas it was stable at room temperature in a dilute solution (10^{-5}—10^{-4} mol/l).§

The most characteristic electronic structural feature of (**2**) is a strong diatropicity observed for the cycloheptatrienylidene ring. This diatropicity is the most significant among the 8-vinylogous heptafulvenes and 8-(fulven-6-yl)heptafulvenes reported so far, the ^{1}H n.m.r. signals of 8-H—11-H of (**2**) being found 1.26 and 0.9 p.p.m. downfield from those of the corresponding seven-membered ring protons of 8-(2,2-dicyanovinyl)heptafulvene[4] and the highly polar 8-(1,2,3,4-tetrachlorofulven-6-yl)heptafulvene,[5] respectively. 15-H of (**2**) appears about 2.0 p.p.m. downfield from the exocyclic methylene protons of the geometrically analogous 8,8-biheptafulvenyl (δ 5.39).[6] Thus, this ground state electronic structural feature of (**2**) must result from a sizeable degree of conjugative interaction between the two chromophores of *p*-tropoquinone methide (**1**) and heptafulvene. In the CNDO/2 calculated MO energy diagram, the HOMOs of (**1**) and heptafulvene are destabilized by 2.77 eV and stabilized by 2.86 eV, respectively, in changing to (**2**) (HOMO: −8.97 eV; next HOMO: −12.70 eV). The LUMO of (**2**) (−0.054 eV), as well as that of (**1**) (−0.030 eV), is at a very low level and has the largest frontier electron density at the 15-C position. Thus the significantly positive reduction potential of (**2**) [E_1 = −0.48 V *vs.* saturated calomel electrode (S.C.E.) in acetonitrile solution] is associated with the *p*-tropoquinone methide component of (**2**).

In its ^{1}H n.m.r. spectrum (CH_2Cl_2) at −70 °C, (**2**) shows a $J_{14,15}$ value of 12.0 Hz and a small chemical shift difference between 1-H and 6-H, and between 2-H and 5-H (Table 1), indicating that this compound exits in an s-*trans*, rather than an s-*cis*, conformation at −70 °C. On warming, the signals for 1,6-H and 2,5-H broaden and collapse at around −40 to

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† Compound (**3**): yellow brown needles, m.p. 131—132 °C, ^{1}H n.m.r. ($CDCl_3$, 200 MHz): δ 2.39 (2H, dd, *J* 6.6 and 6.6 Hz, 9-H), 5.62 (2H, ddd, *J* 9.6, 6.6, and 6.6 Hz, 8,10-H), 6.33 (1H, dd, *J* 9.6 and 5.8 Hz, 11-H), 6.46 (1H, d, *J* 9.6 Hz, 7-H), 6.73 (1H, d, *J* 5.8 Hz, 12-H), 6.70 (1H, d, *J* 15.8 Hz, 14-H), 6.92 (1H, d, *J* 15.8 Hz, 15-H), 7.37 (2H, d, *J* 12.0 Hz, 2,5-H), and 7.58 (2H, d, *J* 12.0 Hz, 1,6-H); *m/z*: 239 (M^+ +1, 21%), 238 (M^+, 100), and 210 (M^+ − CO, 55); i.r. (KBr): 3170, 3040, 1610, 1560, 1460, 1430, 970, and 960 cm^{-1}.

‡ Compound (**4**): red brown needles, m.p. >300 °C, ^{1}H n.m.r.: see Table 1; i.r. (KBr): 3180, 3030, 1600, 1515, 1495, 1460, 1425, 1060, 970, and 860 cm^{-1}; u.v.–vis. (MeCN): λ_{max}/nm (log ε): 227 (4.32), 244 (4.32), 265 (4.11, sh), 390 (4.01, sh), and 493 (4.30).

§ Compound (**2**): ^{1}H n.m.r.: see Table 1; u.v.–vis. (MeCN): λ_{max}/nm (log ε): 230 (4.18, sh), 239 (4.22, sh), 247 (4.26), 255 (4.27), 302 (3.62), 315 (3.67, sh), 370 (3.91), and 585 (4.38). The absorption band at 585 nm showed a hypsochromic shift of 37 nm on changing the solvent to benzene.

Table 1. ^{1}H N.m.r. data (200 MHz) for (**2**) and (**4**).

Compound	Solvent	Temp./°C	1,6-H	2,5-H	8-H—11-H	7,12-H	14-H	15-H
(**2**)	CD_2Cl_2	−35	7.81^a	6.77^a	6.92—7.05	7.10—7.25	6.67^c	7.30^c
		−70	7.86, 7.92^a	6.78, 6.85^a	7.10—7.24	7.25—7.46	6.68^c	7.35^c
(**4**)	CD_3CN	+30	7.95^b	7.42^b	8.74—8.93	9.00—9.15	7.66^d	8.08^d

^{a} J 12.4. ^{b} 11.9. ^{c} J 12.0. ^{d} J 15.4 Hz.

−37 °C, and change into a pair of A_2B_2-type doublets above −35 °C. The values of δ (14,15-H) and $J_{14,15}$ are nearly invariant with temperature while the values of δ (8-H) to δ (11-H) shift downfield by 0.18 p.p.m. on cooling to −70 °C. The equivalent appearance of the quinonoid ring protons at higher temperatures is unequivocally ascribable to the rapid s-*trans* (**2**)–s-*trans* (**2′**) interconversion caused by the rotation about the exocyclic methylene double bond. The rotational barrier ($\Delta G^\ddagger$) calculated from the n.m.r. data is 12.2 kcal/mol (1 cal = 4.184 J). No further material ^{1}H n.m.r. spectral change was observed on cooling from −70 to around −100 °C. In view of the rotational barrier about the intercyclic single bond in 8-(fulven-6-yl)heptafulvene (24.4 kcal/mol),[7] it is not likely that the intercyclic single bond of (**2**) would rotate below −100 °C. These results therefore demonstrate reasonably conclusively that rotation about the exocyclic methylene double bond (15-C–16-C), with the very low energy barrier of 12.2 kcal/mol, takes place in preference to rotation about the single bond (14-C–15-C).¶ The transition state for rotation about the exocyclic methylene double bond would be a zwitterionic species carrying two seven-membered rings twisted with respect to each other at the end of the ethylene bridge, which would be easily accessible by molecular twisting of the charge-separated resonance hybrids (**2a**) or (**2′a**) contributing to the ground state structures (**2**) or (**2′**). Rotation about a double bond in preference to a single bond has not hitherto been observed in vinylogous fulvenes and fulvalenes nor in vinylogous ketones, demonstrating the novel nature of compound (**2**).

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¶ The estimated higher barrier of rotation about the single bond may be associated with the participation of the unstable s-*cis* conformation and with significant geometrical changes in the s-*trans*–s-*cis* interconversion.