

Preparation and Properties of Some Benzotropylium Perchlorates

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The syntheses of a variety of substituted benzotropylium perchlorates, 6,8-polymethylenebenzotropylium perchlorates, and 6,6':8,8'-bispolymethylenedi(benzotropylium perchlorate)s are described. In addition, evidence for the existence of 1a,3-polymethylenebenzohomotropylium cations is presented. By n.m.r. spectroscopy it has been shown that the positive charge (or charges) in these benzotropylium ions is delocalized over both the six- and the seven-membered rings.

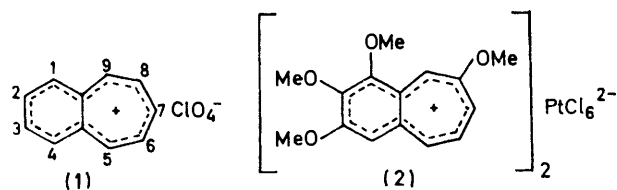
THE first benzotropylium perchlorate (1) was reported by Rennhard in 1955.¹ The same year Eschenmoser and Schaeppi² reported the preparation of 1,2,3,8-tetramethoxybenzotropylium chloroplatinate (2). However, they were unable to isolate the corresponding perchlorate.

We report here the preparation and properties of several new benzotropylium perchlorates and discuss the de-

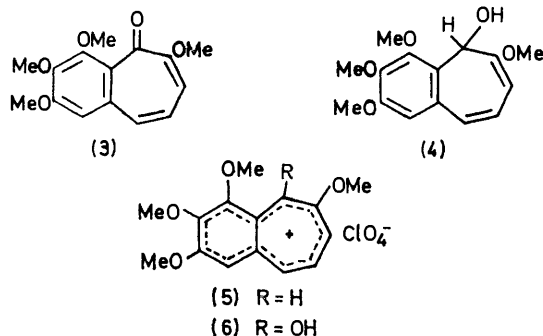
¹ H. Rennhard, *Chem. and Ind.*, 1955, 415.

² A. Eschenmoser and N. Schaeppi, *Helv. Chim. Acta.* 1955, **38**, 1874.

localization of the positive charge within the molecule. The planarity of the tropone ring is also discussed.



1,2,3,8-Tetramethoxybenzotropylium perchlorate (5) was prepared by reduction of 2,3,4,6-tetramethoxy-5H-benzocyclohepten-5-one (3) with lithium aluminium hydride and treatment of the resulting hydroxy-compound (4) with 70% perchloric acid. The earlier



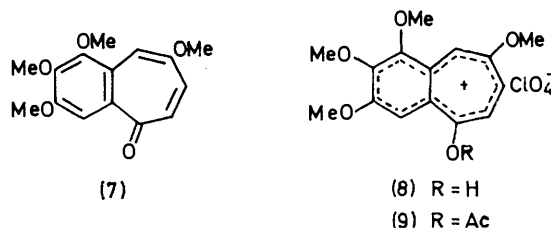
workers^{1,3} presented no direct evidence as to whether the positive charge in benzotropylium salts was delocalized over both rings or just over the seven-membered ring. N.m.r. data for compound (5) indicate that the positive charge is delocalized over both rings, as illustrated by the downfield chemical shift of the resonances due to the substituents. This shift can be attributed to the delocalized positive charge, which decreases the electron density and increases deshielding. The methoxy-resonances for compound (5) are 24 Hz further downfield and the ring proton resonances 90 Hz further downfield than those for compound (3). The u.v. spectrum of compound (5) was consistent with the u.v. spectra of other benzotropylium ions.

Treatment of the benzotropone (3) with perchloric acid afforded the hydroxybenzotropylium perchlorate (6), whose n.m.r. spectrum also showed that the positive charge is delocalized over both rings. The u.v. spectrum of compound (6) was similar to that of (5).

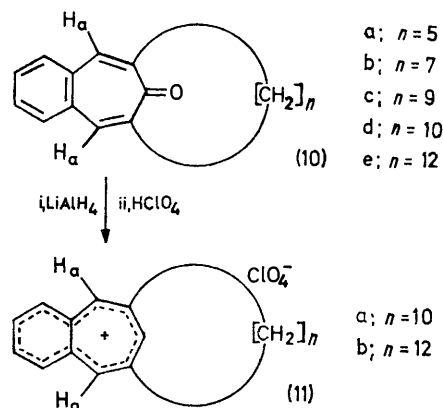
Treatment of compound (4) with chromium trioxide in pyridine² afforded the rearranged benzotropone (7), which on reduction with lithium aluminium hydride followed by treatment with perchloric acid furnished the benzotropylium perchlorate (5). These results are consistent with the fact that the positive charge in structure (5) is delocalized over the seven-membered ring. Treatment of the benzotropone (7) with perchloric acid gave the hydroxybenzotropylium perchlorate (8), recrystallization of which from glacial acetic acid afforded 5-acet-

oxy-1,2,3,8-tetramethoxybenzotropylium perchlorate (9). The n.m.r. spectra of compounds (8) and (9) were consistent with their structures.

A series of 6,8-polymethylenebenzotropylium perchlorates and 6,6':8,8'-bispolymethylenedi(benzotropylium perchlorate)s have been prepared in order to see the



effect of polymethylene bridges on the aromaticity and planarity of the tropylium ions. 6,8-Polymethylenebenzotropones (10) were made by the reaction of equimolar amounts of phthalaldehyde and cyclic ketones. On the basis of i.r. analysis, Kloster-Jensen and co-workers postulated that the tropone ring system in compounds (10) is planar for $n \geq 7$.⁴ From the n.m.r. spectra of these compounds, we substantiated these views. For instance, when $n = 9$ (10c) protons H_a resonate at 7.31 p.p.m., whereas when $n = 5$ (10a) these protons resonate at 6.78 p.p.m. This downfield



shift of the protons in the tropone ring can be attributed to the increased planarity of the system as n is increased. Reduction with lithium aluminium hydride of the carbonyl function in compounds (10) afforded the corresponding alcohols, which on treatment with perchloric acid gave the 6,8-polymethylenebenzotropylium perchlorates (11). The n.m.r. spectra of compounds (11) indicated a further downfield shift in the resonances due to the tropone ring protons H_a (9.2 p.p.m.).⁵

To accomplish the synthesis of 6,6':8,8'-bispolymethylenedi(benzotropylium perchlorate)s [e.g. (15)] the cyclic ketones (12) were prepared from the corresponding diacid chlorides by the procedure reported by Blomquist *et al.*⁶ Condensation of the ketones (12) with phthalaldehyde

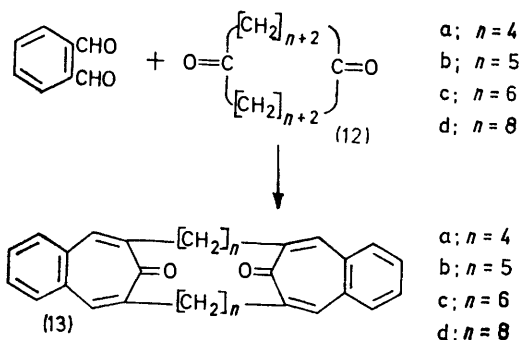
⁵ R. E. Harmon, R. Suder, and S. K. Gupta, *Canad. J. Chem.*, 1970, **48**, 195.

⁶ A. J. Blomquist, J. Prager, and J. Wolinsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1805.

³ L. Buchanan and D. Lockhart, *J. Chem. Soc.*, 1959, 3586.

⁴ Von Else Kloster-Jensen, N. Tarkoy, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, 1956, **39**, 786.

(2 mol. equiv.) in the presence of saturated methanolic sodium hydroxide afforded the 6,6':8,8'-bispolymethylenedi(benzotropone)s (13) in 41–83% yields.⁷ The i.r. spectra of the bisbenzotropones (13) (Table 1) showed



carbonyl absorption at 1595–1605 cm^{-1} , suggesting that the seven-membered tropone ring is planar. When the tropone ring is non-planar, electronic delocalization in it is inhibited and the carbonyl absorption appears at 1650–1700 cm^{-1} , as is the case with 6,8-polymethylenebenzotropones (10) ($n < 7$).

TABLE 1
Spectral data

Compd.	ν_{max} (Nujol) cm^{-1}	$\delta(\text{CD}_3\text{CN})$ (p.p.m.)	λ_{max} (98% H_2SO_4) nm (ϵ)
(5)	1585, 1480, 1081	4.2 (12H, 2 \times s, 4 \times OMe), 5.6–9.2 (5H, m, ArH)	327 (50,000), 373 (5600), 475 (2500)
(6)	1600, 1570, 1080	4.1–4.2 (12H, 3 \times s, 4 \times OMe), 7.4–9.4 (4H, m, ArH), 12.9 (1H, s, OH)	317 (21,300), 363 (2180), 435 (1630)
(9)	1790, 1600, 1090	3.6 (3H, s, OAc), 4.0–4.1 (12H, s, 4 \times OMe), 7.2–8.0 (4H, m, ArH)	323 (27,200), 365 (4380)
(13a)	1623(C=C), 1595(C=O)	1.2–2.9 (16H, m, 8 \times CH_2), 7.0 (4H, s, 4 \times H_a), 7.2–7.6 (8H, m, ArH)	236 (50,200), 264 (40,300), 342 (3070), 359 (1700)
(13b)	1623(C=C), 1595(C=O)	1.0–2.9 (20H, m, 10 \times CH_2), 7.1 (4H, s, 4 \times H_a), 7.5–7.7 (8H, m, ArH)	245 (49,300), 276 (49,000), 341 (2690), 360 (1350)
(13c)	1627(C=C), 1595(C=O)	Not sufficiently soluble	244 (45,500), 277 (44,800), 342 (2170), 360 (1620)
(13d)	1626(C=C), 1605(C=O)	1.0–2.9 (28H, m, 14 \times CH_2), 7.4 (4H, s, 4 \times H_a), 7.5–7.7 (8H, m, ArH)	241 (73,800), 277 (71,000), 340 (4010), 356 (229)
(16)	1640(C=O), 1580(C=C)	1.0–2.6 (18H, m, 9 \times CH_2), 2.9–3.3 (2H, m, cyclopropane CH_2), 6.6 (1H, d, cyclopropane CH), 7.1–7.4 (5H, m, ArH)	

The carbonyl functions in compound (13a) were reduced with lithium aluminium hydride. The resulting

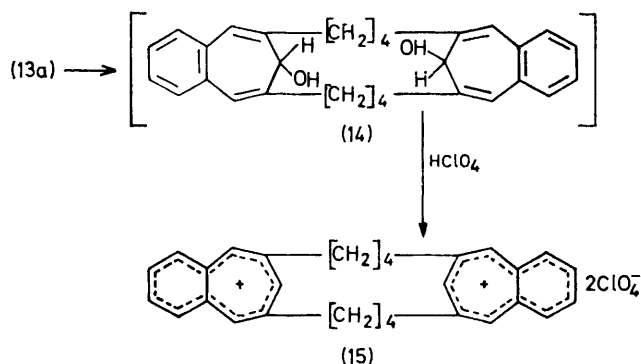
⁷ R. E. Harmon, R. Suder, and S. K. Gupta, *Chem. Comm.*, 1969, 1170.

⁸ R. Pettit and J. D. Holmes, *J. Amer. Chem. Soc.*, 1963, **85**, 2531; O. L. Chapman and R. A. Fugiel, *ibid.*, 1969, **91**, 215.

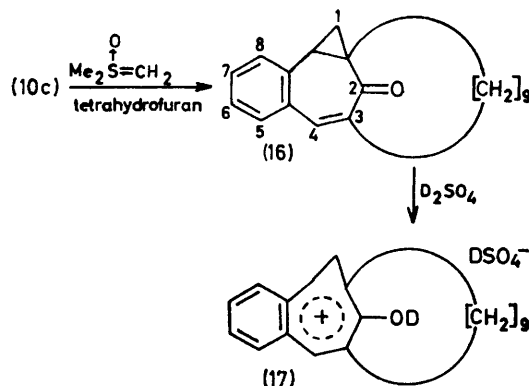
⁹ J. L. Rosenberg, J. E. Mahrer, and R. Pettit, *J. Amer. Chem. Soc.*, 1962, **84**, 2842.

dihydroxy-compound (14), isolated as an oil in 60% yield, was treated with ethereal 70% perchloric acid to afford crystalline 6,6':8,8'-bistetramethylenedi(benzotropylum perchlorate) (15) in 50% overall yield for the two steps.⁷ We were unable to convert the ketones (13b–d) into the corresponding benzotropylum perchlorates because of the poor solubility of the former.

Interest in homoaromaticity and the chemistry of homotropone and homotropylum cations has recently increased.^{8–11} In view of the work of Sugimura *et al.*¹² on benzohomotropylum cations, we treated the benzotropone (10c) with dimethylsulphoxonium methylide¹³



and obtained 1a,3-nonamethylenebenzohomotropone (16) in 50% yield. Its i.r. and n.m.r. spectra were consistent with the structure assigned. The homotropone (16) was treated with deuteriosulphuric acid to give a green solution, the n.m.r. spectrum of which (run



immediately) indicated complete delocalization of the positive charge in structure (17). These results agree with those reported¹² for benzohomotropylum cations.

EXPERIMENTAL

M.p.s were determined with a Thomas–Hoover apparatus and are corrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921, ¹⁰ R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 814.

¹¹ W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 1968, **90**, 814. ¹² Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Letters*, 1971, 91.

¹³ E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1345.

U.S.A. A Beckman IR-8 spectrophotometer was used for recording the i.r. spectra and a Cary-14 spectrophotometer to record the u.v. spectra. The n.m.r. spectra were obtained on a Varian A-60 spectrometer. Procedures for the preparation of compounds (10a—e) and (11a and b) have already been reported.⁵ 2,3,4,6-Tetramethoxy-5H-benzocyclohepten-5-one (3) was obtained by the methylation^{14,15} of commercial 2,3,4,6-tetrahydroxy-5H-benzocyclohepten-5-one.

2,3,4,6-Tetramethoxy-5H-benzocyclohepten-5-ol (4).—A suspension of lithium aluminium hydride (0.32 g, 0.084 mol) in anhydrous ether (25 ml) was added to a solution of compound (3) (2.0 g, 0.0072 mol) in anhydrous ether (25 ml). The mixture was stirred for 3 h at 0° and then for 1 h at room temperature. Decomposition of the complex with water, filtration, and removal of ether under reduced pressure, afforded compound (4) as an oil, whose i.r. spectrum showed the absence of a carbonyl group and the presence of a hydroxy-group (ν_{\max} , 3500s cm^{-1}). Without further purification, this oil was used in the preparation of the perchlorate (5).

1,2,3,8-Tetramethoxybenzotropylium Perchlorate (5).—A solution of compound (4) (2.0 g, 0.0072 mol) in anhydrous ether (25 ml) was treated with 70% perchloric acid (4.0 g, 0.03 mol). After a few min, bright red crystals separated. Filtration, washing with ethyl acetate, and drying yielded the perchlorate (5) (1.5 g, m.p. 130—133° (decomp.); spectral data are given in Table I (Found: C, 50.25; H, 4.6; Cl, 9.9. $\text{C}_{15}\text{H}_{17}\text{ClO}_8$ requires C, 50.0; H, 4.4; Cl, 10.1%).

9-Hydroxy-1,2,3,8-tetramethoxybenzotropylium Perchlorate (6).—Treatment of a suspension of compound (3) in ether with 70% perchloric acid as just described gave yellow-orange crystals (69%) of the perchlorate (6), m.p. 140—142° (decomp.) (from glacial acetic acid) (Found: C, 47.6; H, 4.6; Cl, 9.3. $\text{C}_{15}\text{H}_{17}\text{ClO}_9$ requires C, 47.8; H, 4.55; Cl, 9.3%).

Conversion of the Hydroxy-compound (4) into the Perchlorate (5) via 1,2,3,8-Tetramethoxy-5H-benzocyclohepten-5-one (7).—Treatment of compound (4) with chromium trioxide in pyridine² afforded compound (7) (50%), m.p. 104—105° (lit.,² 106°). A suspension of lithium aluminium hydride (0.2 g, 0.053 mol) in anhydrous ether (20 ml) was added to a solution of compound (7) (0.5 g, 0.0002 mol) in anhydrous ether (20 ml). The mixture was stirred for 3 h at 0° and then for 1 h at room temperature. The usual work-up yielded the corresponding alcohol, which was treated with 70% perchloric acid. The resulting perchlorate was identified as compound (5) by i.r. spectral comparison and mixed m.p. determination with an authentic sample.

5-Hydroxy-1,2,3,8-tetramethoxybenzotropylium Perchlorate (8) and its Acetate (9).—Treatment of an ethereal solution of compound (7) with 70% perchloric acid afforded yellow crystals (62%) of the perchlorate (8), m.p. 164—166° (decomp.), spectra data in Table I. Recrystallisation of the product (8) from glacial acetic acid gave the acetyl derivative (9), m.p. 184—187° (decomp.), n.m.r. data in Table I (Found: C, 48.55; H, 4.65; Cl, 8.6. $\text{C}_{17}\text{H}_{19}\text{ClO}_{10}$ requires C, 48.8; H, 4.55; Cl, 8.55%).

6,6':8,8'-Bispolymethylenedi(benzotropone)s (13a—d).—

The diketones (12a—d) were synthesised⁶ from the corresponding diacid chlorides. Phthalaldehyde (0.4 mol) was condensed with the diketone (12a—d) (0.2 mol) by refluxing (1.5 h) a solution of the two in ethanol (50 ml) in the presence of saturated methanolic sodium hydroxide (50 ml). The precipitate was filtered off and recrystallized (see Table 2).

TABLE 2
Compounds (13a—d)

Com- pound	M.p. (°C)	Yield (%)	Formula	C (%)		H (%)	
				Calc.	Found	Calc.	Found
(13a)	347— 350 *	83	$\text{C}_{30}\text{H}_{28}\text{O}_2$	85.7	85.65	6.4	6.6
(13b)	265— 266 *	54	$\text{C}_{32}\text{H}_{32}\text{O}_2$	85.7	85.9	7.15	7.25
(13c)	264— 265 *	55	$\text{C}_{36}\text{H}_{40}\text{O}_2$	85.75	85.55	7.6	7.85
(13d)	208— 209 †	41	$\text{C}_{38}\text{H}_{44}\text{O}_2, \text{CCl}_4$	70.4	70.3	6.65	6.75

* From tetrahydrofuran. † From carbon tetrachloride.

6,6':8,8'-Bistetramethylenedi(benzotropylium perchlorate) (15).—Lithium aluminium hydride reduction of the bis-benzotropone (13a) as described for the preparation of compound (4) afforded the diol (14) as an oil which did not crystallize. To a solution of the diol (14) (0.5 g, 0.0012 mol) in ether (50 ml), 70% perchloric acid (0.36 g, 0.0025 mol) was added dropwise. After a few min, the product crystallized out. Filtration and recrystallization from glacial acetic acid-acetonitrile afforded the perchlorate (15) (0.45 g, 58%), m.p. 237 (explodes), containing acetic acid as solvent of crystallization (Found: C, 57.7; H, 5.45; Cl, 10.25. $\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{O}_8, 2\text{CH}_3\cdot\text{CO}_2\text{H}$ requires C, 57.75; H, 5.35; Cl, 10.05%), ν_{\max} , 1710 cm^{-1} (AcOH), λ_{\max} , (98% H_2SO_4) 246 (ϵ 87,700), 294 (212,000), 348 (17,800), 361 (5930), and 450 nm (5900) [benzotropylium perchlorate¹⁶ shows λ_{\max} , 282 nm (ϵ 55,000)].

1a,3-Nonamethylenebenzohomotropone (16).—A solution of dimethylsulphoxonium methylide (3.6 mmol) in tetrahydrofuran¹³ was added dropwise to a solution of compound (10c) (5 mmol) in tetrahydrofuran (200 ml) under nitrogen. The solution was stirred at 20° for 6 h. Filtration and removal of the solvent under reduced pressure afforded a white solid, which crystallized from methanol to give the homotropone (16) (0.5 g, 50%), m.p. 131—132° (Found: C, 85.75; H, 8.9. $\text{C}_{21}\text{H}_{26}\text{O}$ requires C, 85.7; H, 8.85%), spectral data in Table I.

1a,3-Nonamethylenebenzohomotropylium Cation (17).—Dissolution of compound (16) (100 mg) in deuteriosulphuric acid (0.4 ml) furnished a green solution, the n.m.r. spectrum of which was studied immediately: δ 1.0—2.4 (18H, m, $9 \times \text{CH}_2$), 3.8—4.4 (2H, m, cyclopropane CH_2), and 7.6—8.0 (6H, m, ArH), consistent with the structure (17) assigned.⁸ Compound (17) was unstable and was not isolated.

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¹⁴ J. Barltrop and J. Nicholson, *J. Chem. Soc.*, 1948, 116.

¹⁵ R. Haworth and B. P. Moore, *J. Chem. Soc.*, 1948, 1409.

¹⁶ A. Eschenmoser, E. Heilbronner, and H. H. Rennhard, *Chem. and Ind.*, 1955, 415.