Tetrahedron Letters,Vol.23,No.46,pp 4797-4800,1982 0040-4039/82/464797-04$03.00/0
Printed in Great Britain

1,4,7,10-TETRAMETHYL-5,6-DIDEHYDRODIBENZO[*a,e*] CYCLOOCTENE. A PRESUMABLY PLANAR FULLY CONJUGATED EIGHT-MEMBERED RING COMPOUND.

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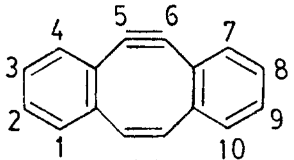
Summary. *The first known stable crystalline derivative of 5,6-didehydrodibenzo[a,e]cyclooctene (1), namely, 1,4,7,10-tetramethyl-5,6-didehydrodibenzo[a,e]cyclooctene (2), was prepared and unequivocally characterised.*

We have been interested in the chemistry of the presumably planar fully conjugated eight-membered carbocycles for almost one decade, and have accordingly prepared a number of these compounds, which possess intriguing chemical and physical properties[3].

One of these planar eight-membered ring compounds, namely, 5,6-didehydrodibenzo[*a,e*]-cyclooctene *(1)*, was isolated and reported in 1974[4]. However, the monoacetylene *(1)* was found to decompose easily[4] as well as to undergo dimerisation and subsequent autoxidation[5], thus posing considerably serious problems in its handling and characterisation. Though through very pain-staking and careful operations, we were able to determine the structure of *(1)* by low temp. X-ray crystallography[6], and to perform several chemical and physical studies[4,7], it would be more desirable to prepare a stable and less reactive derivative of *(1)*.



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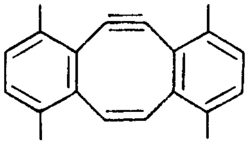
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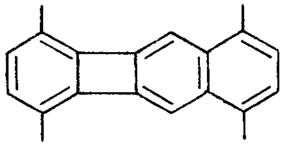
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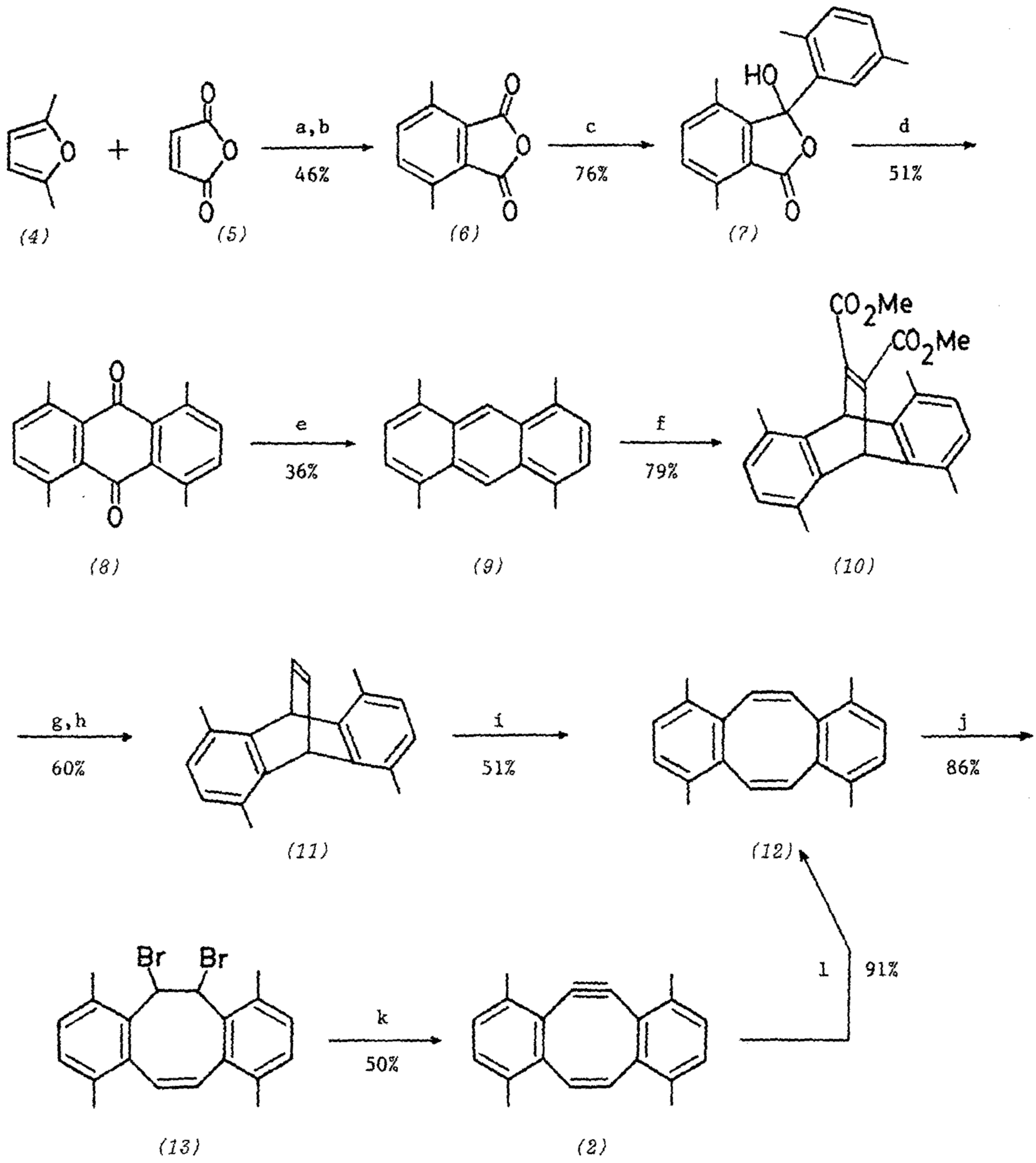
We anticipated that a derivative of *(1)*, which bears four methyl groups at 1,4,7 and 10 positions would sufficiently prevent the molecule from experiencing decomposition and/or dimerisation. Therefore, 1,4,7,10-tetramethyl-5,6-didehydrodibenzo[*a,e*]cyclooctene *(2)* is expected to be comparatively stable and less reactive.

The preparation of the title compound *(2)* through an unexpected pathway was recently reported by us[8]. Nevertheless, an extensive X-ray crystallographic study later revealed that the structure of the compound somehow obtained was actually 1,4,6,9-tetramethylbenzo[*b*]biphenylene *(3)*[9]. We now wish to report a conventional approach, by which the title compound *(2)* was synthesised and unambiguously characterised.

The crystalline adduct obtained from the Diels-Alder reaction of 2,5-dimethylfuran *(4)* and maleic anhydride *(5)* was subjected to conc.H_2SO_4 dehydration, which furnished 3,6-dimethylphthalic anhydride *(6)*[10], m.p. 146-147°C (lit[10]142-143°C). Friedel-Crafts reaction with *p*-xylene and $AlCl_3$ converted the anhydride *(6)* to the pseudo form[11] of 3,6-dimethyl-2-(2,5-dimethylbenzoyl)benzoic acid *(7)*[12], m.p. 145°C (lit[11]150-152°C); ^{1}H-NMR ($CDCl_3$): δ 2.03(s,6H), 2.23(s,3H), 2.53(s,3H), 3.80(br.s,1H), 6.90-7.30(m,5H); MS: M^+ at *m/e* 282. Upon treatment with conc.H_2SO_4, the phthalide *(7)* yielded 1,4,5,8-tetramethylanthraquinone *(8)*[13], m.p. 227°C(dec.)(lit[13]238°C); ^{1}H-NMR (CCl_4): 2.63(s,12H), 7.20(s,4H); IR(KCl): ν 1665 cm^{-1}; MS: M^+ at *m/e* 264. Reduction of *(8)* by Zn in pyridine and HOAc gave 1,4,5,8-tetramethylanthracene *(9)*[13], m.p. 215°C (lit[13]221-222°C); ^{1}H-NMR ($CDCl_3$): δ 2.63(s,12H), 7.03-7.06(d,J=2Hz,4H), 8.46(s,2H); MS: M^+ at *m/e* 234. Diels-Alder reaction between the anthracene *(9)* and dimethyl acetylenedicarboxylate provided 9,10-dihydro-9,10-(1',2'-dicarbomethoxy)etheno-1,4,5,8-tetramethylanthracene *(10)*[14,15], m.p. 224-226°C; ^{1}H-NMR ($CDCl_3$): δ 2.36(s,12H), 3.70(s,6H), 5.85(s,2H), 6.63(s,4H); MS: M^+ at *m/e* 376. The ester *(10)*, when subjected to saponification[16] and copper promoted decarboxylation[16], yielded 9,10-dihydro-9,10-etheno-1,4,5,8-tetramethylanthracene *(11)*[15], m.p. 174-176°C; ^{1}H-NMR (CCl_4): δ 2.41 (s,12H), 5.49-5.62(q,J=3Hz,4Hz,2H), 6.60(s,4H), 6.86-6.99(q,J=3Hz,4Hz,2H); MS: M^+ at *m/e* 260. Photo-rearrangement[17] of the compound *(11)* in THF gave 1,4,7,10-tetramethyldibenzo[*a,e*]-cyclooctene *(12)*[15], m.p. 169-171°C; ^{1}H-NMR ($CDCl_3$): δ 2.18(s,12H), 6.63(s,4H), 6.85(s,4H); MS: M^+ at *m/e* 260. The eight-membered ring structure of *(12)* was established by X-ray crystallography[18] as well as by the smooth catalytic hydrogenation of *(12)* to the known 1,4,7,10-tetramethyl-5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene *(14)*[8], m.p. 149-151°C (lit[8]148-150°C); ^{1}H-NMR ($CDCl_3$): δ 2.20(s,12H), 3.03(s,8H), 6.55(s,4H); MS: M^+ at *m/e* 264. Bromination[4] of *(12)* at 0°C furnished 1,4,7,10-tetramethyl-5,6-dibromo-5,6-dihydrodibenzo[*a,e*]cyclooctene *(13)*[15], m.p. 175-183°C; ^{1}H-NMR ($CDCl_3$): δ 2.06(s,3H), 2.13(s,3H), 2.38(s,3H), 2.54(s,3H), 5.94-6.60(AB, centered at 6.24,J=10Hz,2H), 6.82(s,4H), 7.04(d,J=2Hz,2H); MS: M^+ at *m/e* 418.

Dehydrobromination[4] of the dibromide *(13)* by KO^{t}Bu in THF, followed by usual work up[4], gave the title compound *(2)*[15] in 50% yield. The monoacetylene *(2)* formed yellowish needles (from cold pentane), which decomposed at *ca* 88°C in a sealed capillary upon rapid heating on attempted melting point determination. The electronic spectrum (^{n}Hexane) is similar to that of *(1)*[4], showing λ_{max} at 272nm (ε 80500), 282(87500), 358(3540), 369(sh,3480), 388(sh,2040). The ^{1}H-NMR spectrum ($CDCl_3$) of *(2)* consists of singlets at δ 2.15(12H,methyl), 5.93(2H,olefinic), 6.69(4H,aromatic). When the ^{1}H-NMR spectrum of *(2)* is compared with that of *(12)*, it reveals that the olefinic protons of *(2)* evince a 0.7 ppm upfield shift, which can be attributed to the paratropic effect manifested in the eight-membered ring of the presumably planar fully conjugated acetylene *(2)*. The IR spectrum (KCl) of *(2)* exhibits a weak absorption at ν 2240 cm^{-1}; The



a. Et_2O, 25°C, 4.5h; b. conc.H_2SO_4, -6-0°C, 1h; c. *p*-xylene, $AlCl_3$, 60-65°C, 4h; d. conc.H_2SO_4, 100°C, 1.5h; e. Zn, HOAc, Pyridine, 120°C, 4h; f. dimethyl acetylenedicarboxylate, xylene, 140°C; g. NaOH,H_2O,MeOH; h. Cu, quinoline, 240-260°C, 30min; i. $h\nu$, THF; j. Br_2, CH_2Cl_2 0°C, 20min; k. KO^tBu, THF, 25°C, 30min; l. H_2, PtO_2, EtOAc.

mass spectrum shows M^+ at *m/e* 258. The structure of *(2)* was most convincingly proved by its ready absorption of 1 molar equivalent of H_2 during catalytic hydrogenation over Adam's catalyst to provide *(12)*, m.p. 165-167°C, the spectra data of which are identical in all aspects to an authentic sample of *(12)*.

In conclusion, we have prepared a tetramethyl derivative of *(1)*, which possesses a presumably planar fully conjugated eight-membered ring[3,19]. The monoacetylene *(2)*, in its crystalline state, is remarkably stable and inactive, which is in striking contrast with the property of its parent compound *(1)*. Consequently, a sample of *(2)*, which had been allowed to stand at room temperature (*ca* 28°C) in its crystalline form without protection from air and light for 4 days showed only negligible decomposition in its ^1H-NMR spectrum. On the other hand, the acetylene *(2)* is less stable and rather reactive in Et_2O or $CHCl_3$ solutions, yielding insoluble white solids on standing. This interesting observation supports our view that the four methyl groups of the crystalline *(2)* should exert pronounced steric effect to protect the molecule from undergoing decomposition and/or dimerisation. The reason that the compound *(2)* is less stable in solutions is still unclear. The X-ray crystallographic study of *(2)* is in progress.

Acknowledgments. We would like to thank Mr.Y.H.Law, Department of Chemistry, The Chinese University of Hong Kong, for measuring the accurate masses for all the new compounds. This work is partially supported by a research fund grant, administered by the Royal Society of Chemistry, United Kingdom.

References and Notes.

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(3) For a recent review, see N.Z.Huang and F.Sondheimer, *Acc.Chem.Res.*, 15, 96 (1982).
(4) H.N.C.Wong, P.J.Garratt and F.Sondheimer, *J.Am.Chem.Soc.*, 96, 5604 (1974); H.N.C.Wong and F.Sondheimer, *Tetrahedron*, 37(S1), 99 (1981).
(5) H.N.C.Wong, Ph.D. Thesis, University College London, 1976 and unpublished experiments,see also N.J.Turro, V.Ramamurthy, K.-C.Liu, A.Krebs and R.Kemper, *J.Am.Chem.Soc.*, 98, 6758 (1976); A.Krebs, H.Schmalstieg, O.Jarchow and K.-H.Klaska, *Tetrahedron Lett.*, 21, 3171 (1980); W.Adam, K.Zinner, A.Krebs and H.schmalstieg, *Tetrahedron Lett.*, 22, 4567 (1981).
(6) R.A.G.de Graaff, S.Gorter, C.Romers, H.N.C.Wong and F.Sondheimer, *J.Chem.Soc.,Perkin II*, 478 (1981).
(7) F.Gerson, W.B.Martin,Jr., G.Plattner, F.Sondheimer and H.N.C.Wong, *Helv.Chim.Acta*, 59, 2038 (1976); H.Kojima, A.J.Bard, H.N.C.Wong and F.Sondheimer, *J.Am.Chem.Soc.*, 98, 5560 (1976).
(8) M.-K.Au, T.-W.Siu, T.C.W.Mak and T.-L.Chan, *Tetrahedron Lett.*, 4269 (1978); physical and spectroscopic data of *(3)*: yellow prisms, m.p. 254-255°C; electronic spectrum (n-hexane) λ_{max} 223nm (sh,ε16100), 230(sh,13900), 249(sh,11600), 274 (66300), 282(95700), 294(28500), 307(38800), 355(3400), 375(3500), 395(3980); ^1H-NMR($CDCl_3$): τ 7.87(s,6H), 7.61(s,6H), 3.50(s,2H), 3.11-3.20(m,4H); MS: M^+ at *m/e* 258.
(9) U.Kreever, T.-L.Chan, G.C.Verschoor, E.W.M.Rutten-Keulemans and C.Romers, *Acta Cryst.*, in press.
(10) M.S.Newman and B.T.Lord, *J.Am.Chem.Soc.*, 66, 733 (1944).
(11) W.Carruthers, *J.Chem.Soc.*, 5551 (1963).
(12) M.L.Caspar, J.B.Stothers and N.K.Wilson, *Can.J.Chem.*, 53, 1958 (1975).
(13) W.Carruthers, H.N.M.Stewart, P.G.Hansell and K.M.Kelly, *J.Chem.Soc.(C)*,2607 (1967).
(14) O.Diels and K.Alder, *Ann*, 486, 191 (1931).
(15) Satisfactory elemental analyses and/or high resolution MS were obtained for all new compounds.
(16) H.P.Figeys and A.Dralants, *Tetrahedron*, 28, 3031 (1972).
(17) P.W.Rabideau, J.B.Hamilton and L.Friedman, *J.Am.Chem.Soc.*, 90, 4465 (1968).
(18) Manuscript in preparation.
(19) For a recent report, see F.W.B.Einstein, A.C.Willis, W.R.Cullen and R.L.Soulen, *J.Chem. Soc.,Chem.Comm.*, 526 (1981).

(Received in Japan 12 June 1982)