1,2,3,4-TETRACHLORO-9,10-DEWAR-ANTHRACENE

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Summary: The title compound $\underline{5}$ has been synthesized and its aromatisation to the Kekulé isomer $\underline{7}$ has been measured. From the kinetic data a diradical process is deduced.

Of the valence isomers of benzene, the Dewar isomer, i.e. bicyclo[2.2.0]-hexa-2,5-diene [1], exhibits the least structural change and reverts most easily to the aromatic state. This labile position at the brink of the energy sink of aromaticity provides the bicyclus with continued interest and has led to the synthesis of many derivatives. Of its benzo-condensed analogues, 1,4-Dewar-naphthalene [2a] and 1,4-Dewar-anthracene [2b] have been obtained as well as two 9,10-Dewar-anthracenes stabilized by either 9,10-bridging [2c] or permethylation [2d]. With the title compound $\underline{5}$ we report on the synthesis of a less shielded 9,10-Dewar-isomer of anthracene (scheme 1).

The known tricyclic anhydride $\underline{1}$ [3], obtained from the Diels-Alder reaction of cyclobutadiene with 3,6-dihydro-phthalic anhydride, cycloadds to tetrachloro-o-benzoquinone (CCl_4, $70^{o}C$) with the cyclobutene double bond. Irradiation of the resulting α-diketone $\underline{2}$ with a projector lamp (CH_2Cl_2, $25^{o}C$) splits off the di-oxoethano bridge to give the tetracyclic anhydride $\underline{3}$ [4]. The bis-triethyl-ammonium salt derived from $\underline{3}$ on electrolysis (90% pyridine, $0^{o}C$) forms the Dewar benzene structure in one step, one double bond being introduced by bisde-carboxylation the other by dehydrogenation of the tetrachloro-cyclohexadiene ring[6]. The ice-cold pentane extract of the electrolyte contains a 1:1 mixture of tetrachloro-dihydro-9,10-Dewar-anthracene $\underline{4}$ and its aromatic counterpart $\underline{6}$.

After dehydrogenation of the mixture with dichloro-dicyano-p-benzoquinone ($CHCl_3$
20°C, 35 min) 1,2,3,4-tetrachloro-9,10-Dewar-anthracene 5 and its Kekulé iso-
mer 7 [7] are separated by charge transfer chromatography on silicagel impreg-
nated with 10% s-trinitrobenzene (hexane, -10°C).

Scheme 1
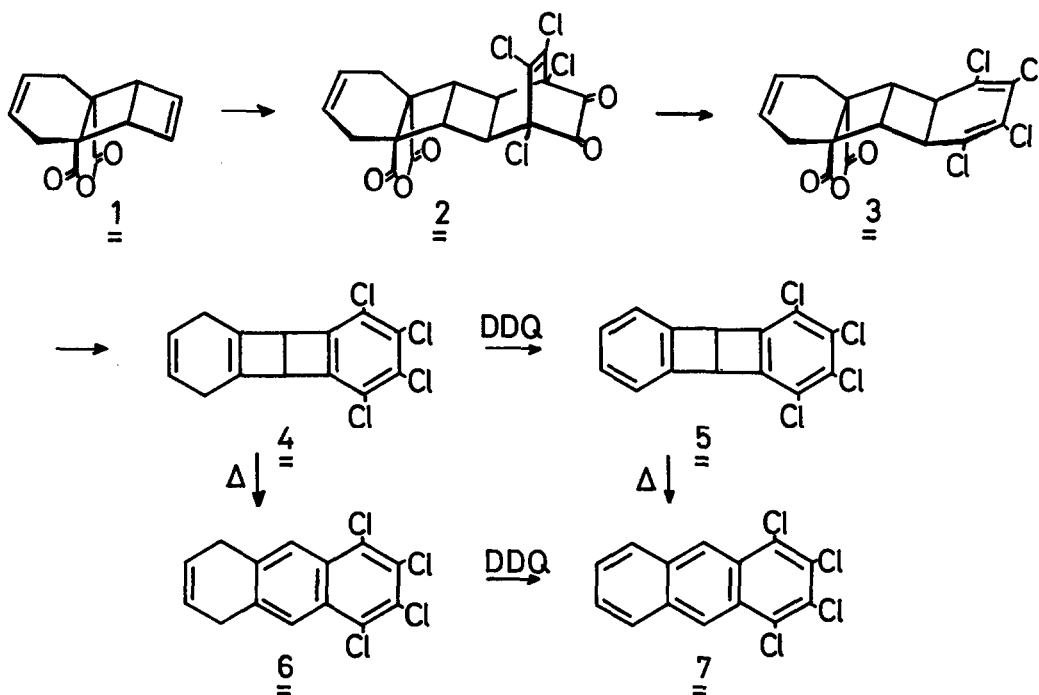
Physical Data of 2, 3, 4, 5 and 6

2   mp 285°; m/e 392 (M^+- 2CO), 216, 78 (base); $\lambda_{max}^{CH_2Cl_2}$ 238 (ϵ 2500), 280
     (1300), 442 nm (260); ν^{KBr} 1865, 1785, 1760, 1570, 920 cm^{-1}; $\delta^{acetone-d_6}$
     6.15 (2H,m), 3.49 (2H,s), 2.65 (4H, AB, $\Delta\nu$ 9.6, J 18 Hz), 2.40 (2H,s).

3   mp 191°; m/e 392 (M^+), 216 (base), 78; $\lambda_{max}^{CH_2Cl_2}$ 290 (sh, ϵ 3700), 301
     (4600), 313 (4200), 327 (2100); ν^{KBr} 1865, 1785, 1615, 915 cm^{-1}; δ^{CDCl_3}
     6.09 (2H,t), 3.67 (2H,m), 3.09 (2H,m), 2.49 (4H, AB, $\Delta\nu$ 12, J 16.5 Hz).

4   δ^{CDCl_3} 5.79 (2H,s), 4.51 (2H,s), 2.70 (4H, AB).

$\underline{5}$ λ_{max}^{hexane} 239 (sh, ε 21000), 260 (1200), 275 (3100), 285 (2200), 296 (2400), 312 (sh, 1800); δ^{CCl_4} 7.27 (4H,m), 5.10 (2H,s).

$\underline{6}$ mp 183°; m/e 318 (M$^+$), 282, 246, 210, 174, 123 (base); δ^{CDCl_3} 8.07 (2H,s) 6.07 (2H,s), 3.63 (4H,s).

The colorless crystals of the title compound $\underline{5}$ are stable at room temperature and transform at 160° without melting into the yellow needles of tetrachloroanthracene $\underline{7}$ (mp 213°). In solution, aromatisation takes place readily at ambient temperature; it was followed in hexane at seven temperatures over the range of 37 to 49°C by monitoring the increase of the 392 nm absorption of $\underline{7}$. Kinetic analysis for the first reaction order by the least squares method yielded the Arrhenius equation:

$$\log k = (13.99 \pm 0.54) - (24470 \pm 790)/2.303 \; RT$$

The activation enthalpy of $\Delta H^{\ddagger} = 23.8 \pm 0.8$ kcal/mol is, within the limits of error, the same as that for the aromatisation of Dewar benzene (23.0 $\pm$ 1.5 kcal/mol [8]) and for Dewar naphthalene (23.0 $\pm$ 0.6 kcal/mol [9]) in accordance with the postulate [10] that the rate determining step in each case is the opening of the central bond to a boat shaped, localized diradical. Certainly, the difference in reaction enthalpy, approximately 26 kcal/mol for the pair Dewar benzene - 9,10-Dewar-anthracene, is not reflected in the height of the activation barriers.

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[4] The tricyclo[4.4.0.0^{2,5}]deca-7,9-diene unit in 3 is thermally more stable
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[6] This aromatisation is possibly due to the neighboring carboxylate groups
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