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HETEROCIRCULENES[1]

A NEW CLASS OF POLYCYCLIC AROMATIC HYDROCARBONS

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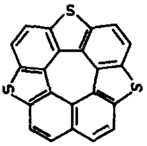
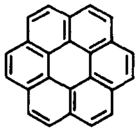
We wish to report the synthesis of a member of a new class of compounds which we would like to call circulenes.[1]

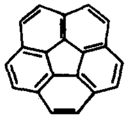
Compound I, whose synthesis is described below can be thought of as a member of a family of compounds whose representatives thus far are limited to coronene (II)[3] and corannulene (III).[4] Our compound I is a [7] circulene, the other members (II and III) are [6] and [5] circulenes respectively.[2]



I



II



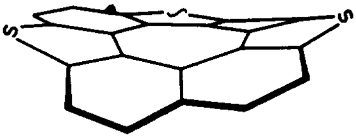
III

In addition to the synthesis of I, we wish to draw attention to the potentially fascinating properties which we envision for this entire family of aromatics.

1. Planarity vs. non-Planarity - depending on the relationship between the outer and inner diameter of these "doughnuts", the circulenes might:
   a. assume a bowl-like shape - as in corannulene (III)[4]
   b. remain planar - as in coronene (II)[3]
   c. become "corrugated" - our compound I in which the outer diameter is too large for planarity (figure 1).

The limits of bond-length adjustments which might keep a "corrugated" circulene planar are not known of course.[5]

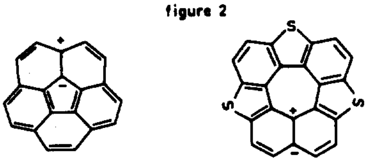
figure 1



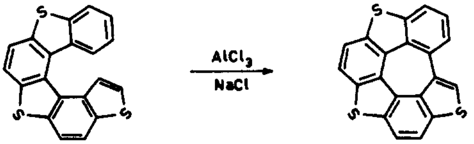
2. Optical activity of a suitably dissymmetric circulene would be prima facie evidence for non-planarity and has been shown to be a very sensitive tool in the investigation of non planar aromatic molecules.[6]

3. Charge distribution - It is evident that charge separated structures in [5] and [7] circulenes might contribute to the resonance hybrid. One should point out that the charge separation in these two classes of molecules can occur in two ways (figure 2).

figure 2



Synthesis of I: When the hexahelicene[7] IV was introduced for several minutes in a $AlCl_3$-NaCl melt of 140°, IV was transformed into V in 95% yield (1). The dehydrohelicene V crystallizes from



(1)

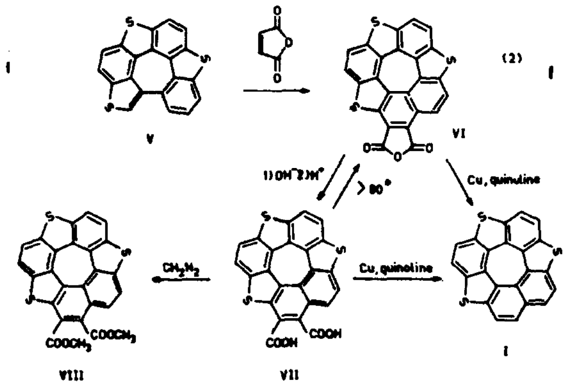
IV V

benzene in small yellow needles m.p. 344-345.[8] M.W. Calcd. for $C_{20}H_8S_3$ 344.5; Found 344 (M.S.). The UV spectrum is shown in figure 3. The NMR spectrum (CS_2) showed a complex pattern between δ 7.6 and δ 8.0 ppm, most characteristic is the absence of shielded protons.[7]

Using essentially a procedure described by Clar and Zander[3], the red anhydride (VI) m.p. above 400°C was obtained in 65% yield when maleic anhydride was allowed to react with V in the presence of chloranil as oxidizing agent (2).

IR 1825, 1772, 1220, 1149, 895, 790 cm^{-1} (no aliphatic CH absorptions). The anhydride VI was highly insoluble but could be sublimated at 350° (10^{-4} mm). When VI was hydrolyzed by boiling in 2N KOH for three hours, an acid VII was obtained, which upon treatment with CH_2N_2 furnished the lightgreen dimethylester VIII; the latter could be recrystallized from CCl_4, m.p. 308-309, IR C=O 1711, 1720 cm^{-1}. NMR CD_2Cl_2 CAT 3H δ 4.06 (s) 3H δ 4.08 (s) 4H δ 7.41 (m) 2H δ 7.54 (m), ppm. The UV spectrum is shown in figure 3. Mass Spectrum in figure 4. Both the diacid VII and dimethylester VIII were thermally unstable and were transformed into the anhydride VI at resp. 80° and above 308°.

Decarboxylation of VI as well as VII in a copper powder-quinoline mixture furnished the heterocoronene I in 25% yield. I was recrystallized from benzene as lightgreen small needles. Decomp. 400-410°. M.W. Calcd. 468.5; Found 468 (M.S.). The UV spectrum is shown in figure 3. NMR CAT, (350 scans) CS_2 shows two broad singlets centered at δ 7.77 and δ 7.72 ppm.



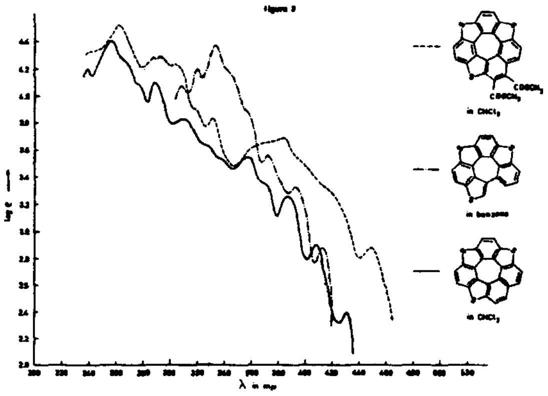
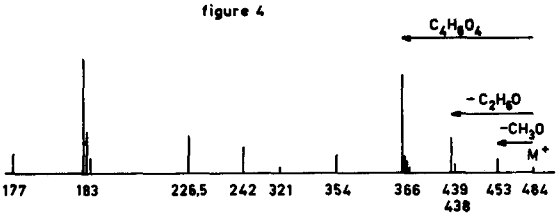


figure 4



177, 183, 226.5, 242 double loaded ions

Mass. Spectrum of VIII

It appears that a general route to [7]circulenes is now available via helicenes.[7] We have recently prepared two more [7] circulenes. Details will be published in a full paper.

Acknowledgement: We thank Dr. M.B. Groen for stimulating discussions.

REFERENCES

1. By analogy with the helicene nomenclature, the class "coronenes" could be subdivided into penta-, hexa- and heptacoronenes and penta-, hexa- and heptaheterocoronenes. Since the term coronene is firmly established for one compound (II), it seems simpler to talk about circulenes and heterocirculenes.
2. The number between brackets indicate the number of (external) aromatic rings and - obviously - the size of the cavity.
3. E. Clar and M. Zander, J. Chem. Soc., 1957, 4616.
4. W.E. Barth and R.G. Lawton, J. Amer. Chem. Soc., 93, 1730, 1971.
   Full credit must go to these authors for their synthesis of the first non-planar compound of this family of compounds.
5. Until rigid experimental proof is available predictions about deviation from planarity seem useless. The endless and partly fruitless disputes around the planarity - non-planarity of o-di-t-butylbenzenes is a case in point. Appreciable bondlengths and angle deviations are well documented.[4]
6. H. Wynberg, Accounts of Chemical Research, 4, 65, 1971.
7. M.B. Groen, H. Schadenberg and H. Wynberg, J. Org. Chem., 36, 2797, 1971.
8. All new compounds gave satisfactory elemental analysis and spectral data.