Tetrahedron Vol. 42, No. 4, pp. 1127 to 1134, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00
Pergamon Press Ltd.

HEXA-PERI-BENZOCORONENE, A CANDIDATE FOR THE ORIGIN OF THE DIFFUSE INTERSTELLAR VISIBLE ABSORPTION BANDS?

W. HENDEL[a)], Z. H. KHAN[a,c)] and W. SCHMIDT[a,b)*)

[a)] Institut für Organische Chemie der Universität, Karlstr. 23, D-8000 München 2
* [b)] Biochemisches Institut für Umweltcarcinogene, Sieker Landstr. 19, D-2070 Ahrensburg
[c)] Department of Physics, Millia Islamia University, New Delhi - 110025, India

(*Received in Germany* 12 *September* 1985)

Abstract - Large polycyclic aromatic hydrocarbons (PAH's) have recently been suggested to be abundant in the interstellar medium surrounding carbon rich stars. To aid in the identification of the species responsible for the astronomical UV and IR data, a new synthesis is reported for hexa-peri-benzocoronene and its dimethyl derivative. The UV, fluorescence, phosphorescence, photoelectron and IR spectra of this extremely stable hydrocarbon are presented and compared with the available astronomical spectra. Experiments useful to check the PAH hypothesis are suggested.

To the growing list of organic molecules identified in the interstellar space,[1] methyl diacetylene has very recently been added.[2] Identification of these small molecules, which bear a dipole moment, is straightforward due to their characteristic microwave emission.

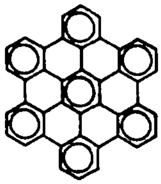
Besides these gas molecules, the interstellar matter contains also dust grains whose presence is indicated by the extinction of the visible and UV light coming from near-by stars. In the visible region, 39 bands have been observed up till now,[3] with bandwidths ranging from 0.1 to 3 nm. An atomic origin for these "diffuse" interstellar bands (or DIB's, as they are called by astronomers) is thus excluded. Although the strongest of these DIB's, at 443 nm, has already been observed in the decade between 1910 and 1920, their origin is still unknown and is considered to be the most outstanding unsolved problem in astronomy.[4]

Early speculations concerning the origin of the DIB mystery centered on linear C_n chains, with n being in the range 5 to 15. This hypothesis, advocated by Douglas,[5] cannot be tested directly because laboratory spectra are lacking except for C_2, C_3 and (possibly) C_4.

The DIB's are accompanied by a continuum centered at 220 nm which may, but need not, originate from the same carrier. Various carriers for this 220 nm feature have been discussed, namely iron, dirty ice, graphite, graphite cores with ice mantles,[6] quartz[7] (particle size 100 to 500 Å), and large polycyclic aromatic hydrocarbons[8] (dimensions about 10 Å).

The recent observation of IR emission[9] from the "Red Rectangle" nebulosity associated with the mass losing carbon star HD 44179 and from object NGC 7027 opens the possibility to resolve the DIB mystery. Superimposed on a broad continuum, which points to hot (~ 600 K) particles, discrete IR features were observed at 3.28, 3.4, 6.2, 7.7, 8.6, 11.3 and 12.7 µm. Léger and Puget[10] were the first to point out that these frequencies are characteristic of polycyclic aromatic hydrocarbons. The IR emission spectrum of coronene ($C_{24}H_{12}$), heated to a peak temperature of 600 K by the absorption of a 6 eV photon, has been computed by these authors, and an impressive (though not perfect) match with the observed frequencies and intensities was noted. Based on theoretical estimates, a species with about 50 carbon atoms would seem to be the most likely candidate.

In his classical papers[11] and two monographs,[12] Clar has stressed the exceptional thermal and photochemical stability of the so-called "fully-benzenoid" hydrocarbons, typified below by hexa-peri-benzocoronene (Ia):



Ia

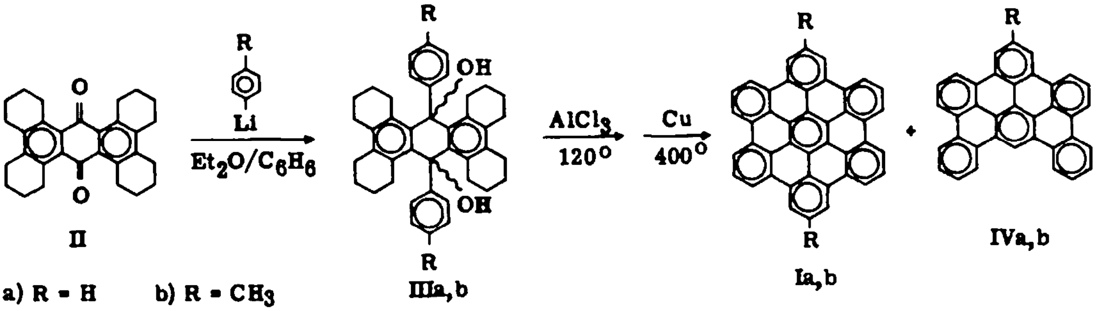
Among the huge PAH variety, compounds belonging to this class are expected to withstand the incessant bombardment by photons ($h\nu < 13.6$ eV) and electrons (< 5 eV) in the interstellar environment.

To determine which species (if only one - perhaps a whole family?) is responsible for the IR emission, laboratory IR spectra of a wide range of PAH's with 40 to 60 carbon atoms are urgently required. Since the carrier(s) of the IR emissions may also provide the clue to the DIB mystery, reliable visible and UV spectra of such molecules including their singly ionized species down to 200 nm are needed.

This paper reports a novel synthesis of Ia and of a dimethyl derivative, plus pertinent spectroscopic data which might help astrophysicists to unravel the DIB and IR features.

Two samples of Ia provided by Professor Clar - one a micro-crystalline yellow powder, the other dark yellow needles - gave identical UV, fluorescence and phosphorescence spectra shown in Fig. 1. In addition to the UV bands already reported by Clar,[12] we observe with both samples a very weak band at 463 nm with $\varepsilon = 220$. This seems to be the 0-0 transition (strictly forbidden in D_{6h} symmetry) of the weak α-band as it coincides with the first recognizable fluorescence band at 462.5 nm; note the perfect mirror symmetry between emission and absorption.

In order to secure this 463 nm band, an alternative synthesis for Ia and a dimethyl derivative Ib was designed, cf. Scheme below. Besides increasing the solubility in organic solvents and boric acid, methyl substitution has the added advantage of intensifying the 0-0 transition of the α-band due to lifting the sixfold symmetry axis.



a) R = H b) R = CH_3

Reaction of the known[13] quinone II with phenyl or p-tolyl lithium afforded the diols IIIa and

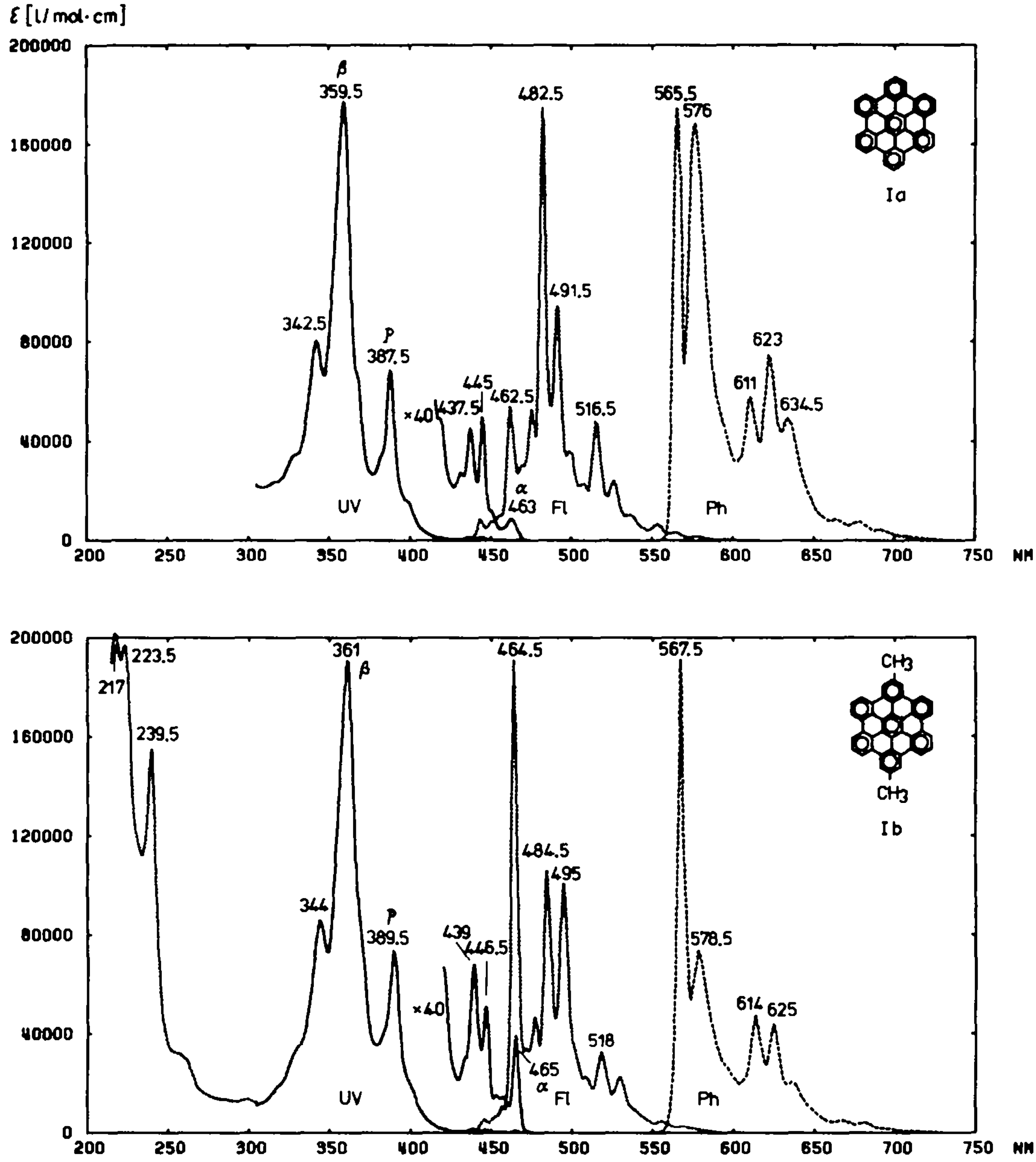


Fig. 1. UV, fluorescence and phosphorescence spectra of Ia and Ib in 1,2,4-trichlorobenzene. UV spectrum of Ib below 305 nm in dioxane. Inserts show weak α-bands on an expanded scale. Phosphorescence spectra taken at 77 K. UV band assignments from Ref. 12.

IIIb whose constitution was confirmed by MS, IR and elemental analysis; yields were between 15 and 50%.[14] Direct pyrolysis with Cu at 400 °C, which smoothly gave the desired hydrocarbons in other cases,[12,14] yielded mainly splitting products. The diols were therefore cyclized in an $AlCl_3/NaCl$ melt (3 min, 120 °C) and then subjected to aromatization with Cu (90 min, 400 °C).

Diol IIIa yielded a mixture of Ia and IVa which could be separated by fractional sublimation and crystallization from trichlorobenzene. Although yields are poor, this synthesis competes favourably with the literature methods[12] in that the starting quinone (four steps from cyclohexanone) is easily prepared in quantity. The spectroscopic properties of Ia agreed in every respect with those of the Clar specimens; in particular, the 463 nm band was confirmed.

The analogous reaction with diol IIIb gave Ib (orange-yellow micro-crystals, mp > 500 °C)

Table. UV, fluorescence and phosphorescence data of Ia and Ib in 1,2,4-trichlorobenzene. λ_{max} values in nm, ε_{max} values (± 5%) in l/mol cm, fluorescence and phosphorescence intensities normalized to 1.0 for most intense band. For procedure to determine ε values see Ref. [15]

Hexa-peri-benzocoronene (Ia)						
UV:	463.0 (220)	445.0 (1230)	437.5 (1130)	387.5 (69000)	359.5 (177000)	342.5 (81000)
Fl:	462.5 (0.31)	475.5 (0.30)	482.5 (1.00)	491.5 (0.54)	516.5 (0.28)	526.5 (0.14)
Ph:	565.5 (1.00)	576.0 (0.97)	611.0 (0.33)	623.0 (0.43)	634.5 (0.28)	
Dimethylhexa-peri-benzocoronene (Ib) [a)]						
UV:	465.0 (980)	446.5 (1270)	439.0 (1700)	389.5 (73300)	361.0 (190000)	344.0 (86000)
Fl:	464.5 (1.00)	477.0 (0.25)	484.5 (0.56)	495.0 (0.53)	518.0 (0.17)	530.0 (0.12)
Ph:	567.5 (1.00)	578.5 (0.39)	614.0 (0.25)	625.0 (0.23)	636.5 (0.11)	

[a)] UV data in dioxane: 239.5 (156000) 223.5 (197000) 217.0 (202000)

and IVb (yellow powder, mp 403 - 405 °C). Yields for Ib and IVb, after separation and purification, were 0.4 and 2 %, respectively. The presence of the two methyl groups in Ib was confirmed by MS (base peak at m/e = 550) and IR (aliphatic stretch in KBr at 2912/2849 cm^{-1}). All bands in the UV, fluorescence and phosphorescence spectra are shifted to the red by 1 to 2 nm and, most importantly, the 0-0 transitions are significantly enhanced (Fig. 1 and Table), as expected on the basis of the lower molecular symmetry, namely D_{2h} vs. D_{6h}. This demonstrates again that the 463 nm feature in the UV spectrum of Ia is real, i.e. it is neither a hot band to the sharp doublet at 445/437.5 nm nor due to an impurity. Low-temperature fluorescence excitation and emission spectra, not shown here, further strengthen this conclusion.

Diols were also prepared from m,m'-xylyl and p-tert.-butylphenyl lithium. However, dealkylation prevails under the harsh conditions of the cyclization step so that no pure products were obtained yet. Milder methods for cyclization are at present under scrutiny.

The enhanced solubility of Ib, compared to Ia, enabled us to record the UV spectrum in dioxane down to 210 nm. There is a wide window between the β-band at 361 nm and a group of bands centered near 220 nm. Other annelated coronenes show a similar behaviour.

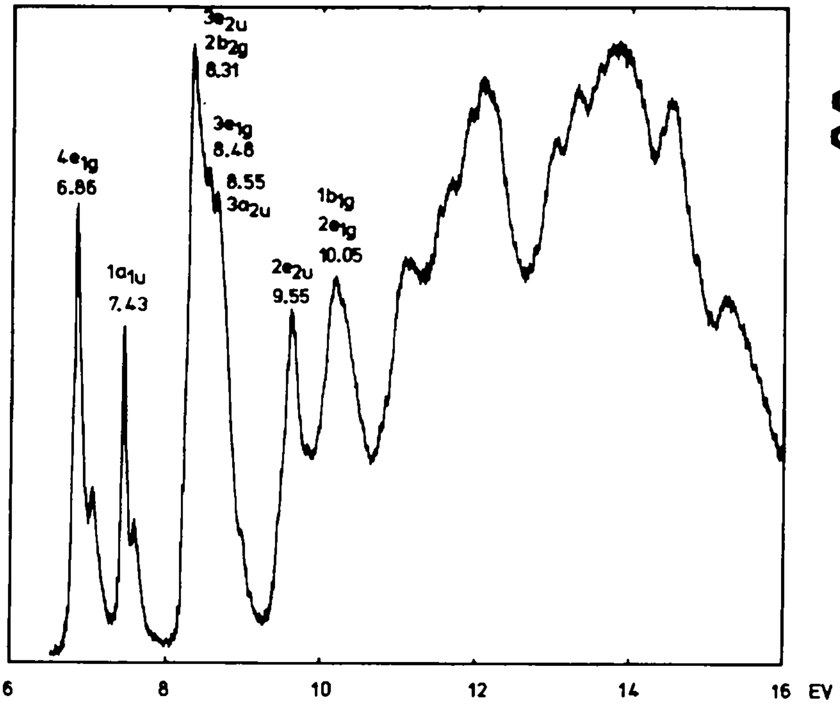
In connection with the DIB mystery, the UV spectrum of the radical cation of Ia would be instrumental. Léger et al.[16] estimate that a considerable fraction (75 % in the case of coronene) of the cosmic abundance of PAH's is singly ionized in the interstellar radiation field. In view of its lower first IP (6.86 eV vs. 7.29 eV for coronene,[17] vide infra), this fraction may be even higher for Ia. Attempts to generate the radical cation of Ia in a boric acid matrix by UV irradiation were of no avail due to poor solubility in this medium. However, previous work in our as well as other laboratories[18,19] has shown that the sharp I-type transitions, which dominate in the visible region and which correspond to transitions from doubly occupied π-levels to the singly occupied one, can be predicted from the measured IP's according to

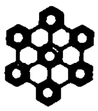
$$E_{I,n} = IP_n - IP_1 \qquad (n = 2, 3, 4 \cdots).$$

Similarly, the A-type band of the radical cation, which is usually the most intense one in the visible region and which is due to the HOMO-LUMO transition, can be estimated[19] as follows:

$$E_A = -6.017 + 1.181\, IP_1.$$

To this end, the photoelectron spectrum of Ia was recorded (Fig. 2) and assigned on the basis of





Ia

Fig. 2. Gas-phase photoelectron spectrum of Ia, recorded at 450 °C. Symmetry labels (below 10.7 eV) refer to point group D_{6h}.

Koopmans' theorem using the four-parameter Hückel model described in Ref. 17. This model was calibrated with the photoelectron data of about 250 polycyclic aromatics and allows the first and higher π-IP's to be calculated within ±0.10 eV. Agreement with the observed peak positions is satisfactory, and the assignments set out in Fig. 2 are in accord with π-SCF theories (e.g. PPP), except for the central 8.3 eV band which is due to six orbitals with Hückel eigenvalue coefficients $x_i = 1$; therefore, the computed level ordering depends critically on the parametrization and the geometry used, and is hence provisional.

Neglecting matrix effects, which previous experience has shown to be small, I-type transitions are predicted, on the basis of the photoelectron data, to come at 2175, 855, ~765, ~734, 461 and 389 nm. The 461 nm band, which corresponds to the transition $4e_{1g} \leftarrow 2e_{2u}$, is predicted to be electrically dipole allowed. It should be noted, however, that several of these predicted values are uncertain, as they rest upon a correct identification of the IP's (e.g. the 8.3 eV band, vide supra), and upon the extent of configurational mixing which may be significant for the higher-energy optical transitions. Owing to the low first IP of 6.86 eV, the A-type band in Ia must be considerably red-shifted relative to coronene where it is found at 468 nm in boric acid.[19] The predicted value, 595 nm, is a rough estimate only as configuration interaction in the radical cation may modify the HOMO-LUMO transition energy in an unpredictable manner.

A unique property of neutral Ia, which would be useful for identification purposes, lies in its extremely intense and long-lived phosphorescence. At 77 K in trichlorobenzene, $\tau_{1/2}$ is 2.79 ± 0.06 sec for Ia, and 2.71 ± 0.08 sec for Ib. In the gaseous state and the absence of an external heavy-atom perturber, life-times are expected to be even longer. However, attention is drawn to the fact that the shape of the phosphorescence band depends not only on substitution (cf. Fig. 1), but also on the temperature and the environment; band shapes would certainly be very different if Ia were in the gaseous state or attached to the surface of dust grains in the interstellar medium.

In a recent high-resolution optical study[20] of HD 44179 and its associated nebulosity (the "Red Rectangle"), sharp emission features were observed at 580.0, 582.6, 585.3, 588.5, 591.4 and 594.0 nm; these were followed by a broad-band red emission (hence the name) centered at ~640 nm. The authors[20] note that neither the sharp features nor the red emission can be identified with transitions in any known atomic or molecular (e.g. H_2O^+, FeO, CaCl, C_2, C_3) species. Since this nebula shows the IR emissions characteristic of PAH's, it is tempting to ascribe the above emission to fluorescence or phosphorescence of this very class of compounds.[21] It is an open question, however, whether the PAH's are neutral or singly ionized in the nebular medium surrounding HD 44179. In laboratory spectra, benzenoid hydrocarbons emit exclusively from the first excited state (Kasha's rule). For the radical cation of Ia with its degenerate HOMO (cf. Fig. 2), the first excited state would be degenerate or nearly so (Jahn-Teller distortion) with the ground state, so emission would occur in the far-IR and would be very feeble as the transition is dipole forbidden. For compounds of lower symmetry lacking this HOMO degeneracy, the lowest energy transition is still in the IR as the π-levels of larger PAH's bunch closely.[22] It is to be noted, however, that in the gaseous state, where internal conversion is hampered, emission may occur from higher excited states of the cation. This question could be solved by looking for visible resonance fluorescence in photoelectron experiments.

Clar described Ia as a "pale yellow hydrocarbon of great stability. Its melting point could not be determined because the melting-point tube melted long before the hydrocarbon".[12] In keeping with this description, no skeletal fragmentation is observed in the mass spectrum, within the limits of detection (0.5% of base peak, at 395 °C). The $M^+ - 2$ peak, due to the loss of two hydrogen atoms, is exceptionally weak (12% of M^+ peak), and both M^{++} and M^{+++} are clearly visible. Ia can be sublimed, without decomposition, at red heat in a quartz test tube which is open to the air.

The IR spectrum of Ia in KBr shows prominent bands at 3080, 3040, 3008, 1608, 1589, 1495, 1412, 1378, 1228, 880, 760 and 738 cm^{-1}. The latter two, which are the most intense ones, are interpreted as the "trio" (three adjacent H atoms on an aromatic ring[23]) out-of-plane C-H modes. Comparison with recent low-resolution IRAS maps[24] of various galactic and extragalactic nebulae, including the bright HD 44179 and NGC 7027 sources,[9] reveals broad agreement as far as the typical PAH signature is concerned, but differences in the finer details, namely the out-of-plane C-H region. Although spectral variations from source to source in the IRAS data are evident, the 11.3 μm (885 cm^{-1}) emission feature is always more intense than that at 12.7 μm (787 cm^{-1}). This places important constraints on the topology of the species responsible for the emission. The 885 cm^{-1} band can only arise from "solo" H atoms, whereas the 787 cm^{-1} band points to either "duo" or "trio" H atoms (these spectral ranges overlap and are not readily distinguished in practice). Generally, solo bands are more intense than duo bands; for example, in ovalene[17] (2 solo and 12 duo H atoms) and dicoronylene[15] (4 solo and 16 duo H atoms), both bands assume roughly the same integrated intensity. Taken together, the astronomical IR data are indicative of peri-condensed PAH's with a compact, disk-like shape such as encountered in circumanthracene[17] or circumcoronene.[25] However, direct comparison with laboratory spectra is rendered difficult because the astronomical species may be partly ionized or bound to graphitic particles. Absorption of a photon, besides leading to radical cation formation, may also result in C-H rupture which further modifies the IR frequencies. These and other open questions[10,26] call for pertinent laboratory experiments.

No definite conclusions regarding the carrier(s) of the peculiar DIB and IR features can be drawn at this stage. Obviously, the astronomical data cannot be ascribed to a single known PAH species. We emphasize, however, that a systematic and comprehensive screening of the spectra of large hydrocarbons (including their radical cations) has not yet been done. On top of this, the mode of formation of PAH's remains to be elucidated by simulated laboratory experiments. In Nature, these are presumably formed in the carbon-rich outflow from planetary nebulae and carbon-rich Miras, i.e. from C_2, C_3, carbonaceous or graphitic particles, and abundant hydrogen.

Acknowledgements. One of the authors (W. S.) wishes to thank Alain Léger and Louis d'Hendecourt (Université Paris VII) for exchange of ideas and for introducing him into the field of interstellar chemistry. Professor E. Clar (University of Glasgow, Scotland) kindly provided specimens of hexa-peri-benzocoronene. Support of this work was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

EXPERIMENTAL SECTION

Fluorescence and phosphorescence spectra were measured in the Ratio mode with an SPF-500 instrument of American Instrument Co., using a 250 W xenon source, and are semi-corrected. The photoelectron spectrum of Ia was recorded with model 0078 of Helectros Developments, Beaconsfield (England), and was calibrated using the He^+ peak at 4.98 eV and the Ar doublet.

The synthesis of the diols is exemplified below for IIIb.

To a suspension of 6.37 g (15 mmol) of quinone II in 80 ml of dry benzene was added, with magnetic stirring and under dry nitrogen, a solution of p-tolyl lithium prepared from 7.70 g (45 mmol) of p-bromo toluene in 100 ml of dry ether and 31 ml (49.6 mmol, 1.6 molar) of n-butyl lithium in hexane. After stirring the deep red mixture for 15 min, the ether was driven off in a stream of dry nitrogen, and the reaction was completed by heating to reflux for another 15 min. Hydrolysis with dilute acetic acid yielded a pale yellow precipitate, mp 282.5 - 284.5 °C (from benzene). Yields varied between 29 and 46 %. Colour in conc. H_2SO_4 blue-violet. - Analysis calc. for $C_{44}H_{48}O_2$: C 86.80, H 7.95; found C 86.74, H 8.29%. - IR (KBr, cm^{-1}): 3520 (O-H stretch), 3020 (arom. C-H stretch), 2922/2868 (aliph. C-H stretch), 1147 (C-O stretch), 808 (C-H out-of-plane). - MS (180 - 190 °C, 70 eV, m/e): 590 (M^+ - H_2O), 572 (M^+ - 2 H_2O), 499 (M^+ - H_2O - C_7H_7), 481 (M^+ - 2 H_2O - C_7H_7).

The diol prepared in same manner from m, m'-xylyl lithium and quinone II was obtained in 24% yield, mp 324 - 325°C dec. (from benzene/petrol ether). Colour in conc. H_2SO_4 red. - Analysis calc. for $C_{46}H_{52}O_2$: C 86.75, H 8.23; found C 86.49, H 8.07%. - IR (KBr, cm^{-1}): 3622 (O-H stretch), 2923/2864 (aliph. C-H stretch), 1139 (C-O stretch), 843/819 (C-H out-of-plane). MS (225 °C, 70 eV, m/e): 636 (M^+), 618 (M^+ - H_2O), 600 (M^+ - 2 H_2O), 531 (M^+ - C_8H_9), 513 (M^+ - H_2O - C_8H_9).

The diol obtained from p-tert.-butyl-phenyl lithium and quinone II in 18 - 31% yield had mp 290 - 291.5 °C dec. (from xylene). Colour in conc. H_2SO_4 pink-violet. - Analysis calc. for $C_{50}H_{60}O_2$: C 86.66, H 8.73; found C 86.18, H 8.62%. - IR (KBr, cm^{-1}): 3528 (O-H stretch), 3033 (arom. C-H stretch), 2929/2863 (aliph. C-H stretch), 821 (C-H out-of-plane). - MS (200 - 210 °C, 70 eV, m/e): 674 (M^+ - H_2O), 656 (M^+ - 2 H_2O), 617 (M^+ - H_2O - C_4H_9), 599 (M^+ - 2 H_2O - C_4H_9), 523 (M^+ - 2 H_2O - $C_{10}H_{13}$).

The cyclization and aromatization of the diols is exemplified below for the reaction leading from IIIb to the hydrocarbons Ib and IVb.

An intimate mixture of 9.42 g of diol IIIb and 9.42 g of NaCl is added, with stirring, to a melt of 75.4 g of $AlCl_3$ and 9.42 g of NaCl held at 120 °C. Stirring was continued for 3 min. After cooling, the dark melt was decomposed with dilute HCl, and the red-brown precipitate was washed with water, dilute ammonia, and water again. The crude product (8.33 g) was intimately mixed with 33.3 g of Cu powder and heated under CO_2 to 400 °C for 90 min. Subsequent sublimation at 600 °C/0.01 mbar yielded 1.28 g of crude product. This was extracted with benzene to remove splitting products and crystallized from 1, 2, 4-trichlorobenzene, giving 334 mg of a mixture of Ib and IVb. Separation was achieved by repeated fractional sublimation and fractional recrystallization from trichlorobenzene, resulting in 3.6 mg of Ib (0.4% based on diol) and 154 mg of IVb (2%), both in a spectroscopically pure state.

Ib forms orange-yellow micro-crystals, mp > 500 °C. - For UV data see Fig. 1 and Table. - IR (KBr, cm^{-1}): 3072 (arom. C-H stretch), 2912/2849 (aliph. C-H stretch), 1624/1607/1592 (C=C stretch), 1381 (CH_3 deform.), 850/815/783/763/741 (C-H out-of-plane). - MS (400 °C, 70 eV, m/e): 550 (M^+), 536 (M^+ - CH_2), 522 (M^+ - 2 CH_2), 275 (M^{++}), 183.3 (M^{+++}).

IVb was obtained as a yellow powder, mp 403 - 405 °C (parent system[12] 434 - 436 °C). - Analysis calc. for $C_{37}H_{20}$: C 95.66, H 4.34; found C 95.73, H 4.52%. - UV (dioxane, λ_{max} in nm, log ε): 428 (2.75), 413 (2.96), 404.5 (3.04), 373 (4.16), 361.5 (4.59), 329.5 (4.99), 315.5 (4.77), 302 (4.75), 289 (4.50), 237 (4.96), 223.5 (5.02). - IR (KBr, cm^{-1}): 3064 (arom. C-H stretch), 2961/2846 (aliph. C-H stretch), 1616/1585 (C=C stretch), 1385 (CH_3 deform.), 828/788/748 (C-H out-of-plane). - MS (210 °C, 70 eV, m/e): 464 (M^+), 450 (M^+ - CH_2), 232 (M^{++}).

The analogous reaction with the diol carrying two tert.-butyl groups (3.67 g) yielded 16.4 mg of Ia and 73.1 mg of IVa. The hydrocarbons with tert.-butyl groups were seen in the MS, but could not be isolated as pure substances. Ia and IVa obtained in this experiment (and also starting with diol IIIa) were identical to the compounds described by Clar[12] (see text above).

REFERENCE LIST

1 Duley, W.W., Williams, D.A., Interstellar Chemistry, Academic Press, New York, 1984.

2 Walmsley, C.M., Jewell, P.R., Snyder, L.E., Winnewisser, G., Astron. Astrophys. 1984, **134**, L11.

3 Herbig, G.H., Z. Astrophys. 1966, **64**, 512; Astrophys. J. 1975, **196**, 129.

4 Huffman, D.R., Adv. Phys. 1977, **26**, 127.

5 Douglas, A.E., Nature 1977, **269**, 130.

6 Krishna Swamy, K.S., O'Dell, C.R., Astrophys. J. 1967, **147**, 937.

7 Knacke, R.F., Nature 1968, **217**, 44.

8 Platt, J.R., Astrophys. J. 1956, **123**, 486; Donn, B., ibid. 1968, **152**, L129.

9 Allamandola, L.J., in: Galactic and Extragalactic IR Spectroscopy, Eds. Kessler, M.F., Phillips, J.P., Reidel, Holland, 1984; Willner, S.P., loc. cit.

10 Léger, A., Puget, J.L., Astron. Astrophys. 1984, **137**, L5; Pujet, J.L., Léger, A., Boulanger, F., ibid. 1985, **142**, L19.

11 Clar, E., Zander, M., J. Chem. Soc. 1958, 1861; Clar, E., Ironside, C.T., Zander, M., ibid. 1959, 142.

12 Clar, E., Polycyclic Hydrocarbons, Academic Press, New York, 1964; Clar, E., The Aromatic Sextet, Wiley, London, 1972.

13 Backer, H.J., Strating, J., Huisman, L.H.H., Rec. Trav. Chim. Pays-Bas 1939, **58**, 761; Bergmann, E., Eschinazi, H.E., Neeman, M., J. Org. Chem. 1943, **8**, 179.

14 Hendel, W., diploma work, Universität München, 1982.

15 Lempka, H.J., Obenland, S., Schmidt, W., Chem. Phys. 1985, **96**, 349.

16 Léger, A., d'Hendecourt, L., Astron. Astrophys. 1985, **146**, 81.

17 Clar, E., Robertson, J.M., Schlögl, R., Schmidt, W., J. Amer. Chem. Soc. 1981, **103**, 1320.

18 Shida, T., Nosaka, Y., Kato, T., J. Phys. Chem. 1978, **82**, 695.

19 Khan, Z.H., Z. Naturforsch. 1984, **39A**, 668; Khan, Z.H., Schmidt, W., J. Mol. Struct., submitted.

20 Schmidt, G.D., Cohen, M., Margon, B., Astrophys. J. 1980, **239**, L133.

21 d'Hendecourt, L.B., Léger, A., Olofsson, G., Schmidt, W., Astron. Astrophys., submitted.

22 Boschi, R., Clar, E., Schmidt, W., J. Chem. Phys. 1974, **60**, 4406.

23 Groenewege, M.P., Colloquium Spectroscopicum Internationale VI (Amsterdam, 1956), Pergamon Press, London, 1956; Zander, M., Erdöl Kohle 1962, **15**, 362.

24 IRAS (Infrared Astronomical Satellite) data base, presented in part by De Muizon, M., Habing, H.J., Proc. of the VIII European Regional IAU Meeting, Toulouse, France, 1985.

25 For synthetic attempts see Ref.[14].

26 Désert, F.X., Boulanger, F., Léger, A., Puget, J.L., Sellgren, K., Astron. Astrophys., submitted.