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FULVENES AND THERMOCHROMIC ETHYLENES—XXXVI[1]

NMR STUDIES IN THE SERIES OF 2,3,6,7-DIBENZOHEPTAFULVENE AND 2,3,6,7-DIBENZOTROPONE

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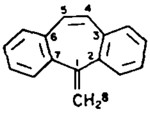
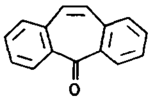
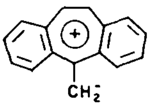
It is well known that the properties of the heptafulvenes are less in accord with the predictions of the LCAO theory than those of the fulvenes.[2–4] In order to determine the degree of "pseudo-aromaticity" in the systems e.g., 2,3,6,7-dibenzoheptafulvene (A) or 2,3,6,7-dibenzotropone (B), the dipole moments and the UV spectra have been investigated. These methods indicate essentially the presence of tropylium ion structures (A′,B′) and to a lesser extent resonance structures in which the π-electrons are associated with the whole heptafulvene system. These structures are identifiable by means of the NMR spectrum, as the following considerations show:



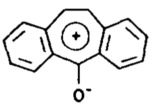
A



B



A′



B′

The hydrogen atoms in positions 4 and 5 as well as 8 are easily distinguishable, the latter because they do not appear in the spectrum of the tropones (B). The preparation of 8-substituted derivatives of I permits the determination of the influence of the substituent on the remaining hydrogen atom at C_8 and on the hydrogen atoms at C_4 and C_5. Equally, the comparison of the system (A) with its benzologs permits a study of the influence of the absorption of the hydrogen atoms at C_4 and C_5–when the annelation takes place far from the central double bond—and of the hydrogen atoms at C_8—if annelation takes place far from the semicyclic double bond (C_1–C_8). In general, differences in the degree of aromaticity can only be established by NMR spectroscopy if the points of difference in the constitution of the compounds to be compared are far removed from the hydrogen atoms whose absorptions are being studied; otherwise these absorptions may be influenced by inductive or steric effects which are not necessarily related to the aromatic character of the molecule.

One can foresee that an increase of the aromatic character of the system studied will lead to an absorption of H_4 and H_5 at lower field and to an absorption of H_8 at higher field. Conversely, an enhancement of the polar structure A′ by substitution

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[1] Part XXXV: M. Rabinovitz, I. Agranat and E. D. Bergmann, *Tetrahedron Letters* 1265 (1965).

[2] G. Berthier and B. Pullman, *Trans. Faraday Soc.* **45**, 484 (1949).

[3] E. D. Bergmann, E. Fischev, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. Soc. Chim. Fr.* **18**, 684 (1951).

[4] A. Julg, *J. Chim. Phys.* **52**, 50 (1955).

at C_8 will lead to an absorption of H_8 at higher field, but not necessarily to an absorption at H_4 and H_5 at lower field.

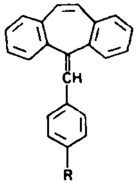
It seemed, therefore, of interest to study a series of compounds of type A and B and of related substances.[5]

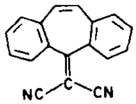
Materials and methods. The NMR spectra were measured in $CDCl_3$ at room temp with a Varian A-60 instrument. Tetramethylsilane served as internal standard.
The following substances have been tested:

2,3,6,7-*Dibenzoheptafulvene* (A) from pet. ether, m.p. 144–145°.[3]
8-*Phenyl*-2,3,6,7-*dibenzoheptafulvene* (I, R = H), b.p. 210° (0·1 mm).[3]
8-(p-*Chlorophenyl*)-2,3,6,7-*dibenzoheptafulvene* (I, R = Cl), from pet. ether, m.p. 155°.[3]
8,8-*Dicyano*-2,3,6,7-*dibenzoheptafulvene* (II), from butanol, m.p. 240°.[6]
8-*Phenyl*-2,3,6,7-*tribenzoheptafulvene* (III), from EtOH, m.p. 152–153°.[7]
5H-*Dibenzo* [a, d] *cyclohepten-5-one* (B), from pet. ether, m.p. 90–91°.[8]
5H-*Benzo* [a] *naphtho* [1, 2-d] *cyclohepten-5-one* (IV), from benzene-ligroin, m.p. 136–137°.[9]
5H-*Dinaphtho* [2,1-a: 1′,2′-d] *cyclohepten-5-one* (V), from butanol, m.p. 245°.[9]
9-*Hydroxymethyl*-2,3,6,7-*dibenzocyclohepta*-2,4,6-*triene* (VII), from cyclohexane, m.p. 88°.[10]
Triphenylethylene was prepared by the standard method.

cis-1,2-*Di*-(2-*naphthyl*)-*ethylene* (VI). Although a known compound,[11] it was prepared by the following method in this laboratory:[6] The 1,2-di-(2-naphthyl)-acrylic acid, m.p. 215°, obtained from 2-naphthaldehyde and 2-naphthylacetic acid in the presence of triethylamine and acetic anhydride, gave upon decarboxylation (with Cu in quinoline) both the *trans*-isomer of VI (m.p. 260°, from benzene) and the *cis*-form (VI) (m.p. 106°, from EtOH).

Table 1 summarizes the measurements and indicates also the dipole moments of the compounds, as far as they have been measured.


I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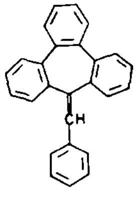
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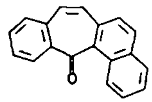
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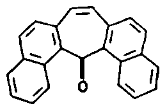
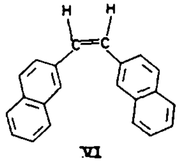
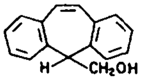

V


VI


VII

DISCUSSION

1. *Absorption of* H_8. Whilst the shift of the absorption to lower field, caused by phenylation of A to I (R = H), is approximately the same as that caused by phenylation of 1,1-diphenylethylene to triphenylethylene, the absorption of H_8 in compound A is different from that of the olefinic hydrogen atoms in 1,1-diphenylethylene, indicating that H_8 in A is more acidic and, therefore, the 1,8-double bond in this compound more polar than the corresponding double bond in 1,1-diphenylethylene.

[5] For the relation of NMR spectra and dipole moments, see E. M. Evleth, J. A. Berson and S. L. Manatt, *Tetrahedron Letters* 3087 (1964).

[6] E. D. Bergmann and I. Agranat, unpublished results.

[7] E. D. Bergmann and J. Klein, *J. Org. Chem.* **23**, 512 (1958).

[8] E. D. Bergmann and R. Ikan, *J. Org. Chem.* **28**, 3341 (1963).

[9] I. Agranat and E. D. Bergmann, *Israel J. Chem.* **1**, 246 (1963).

[10] E. D. Bergmann and M. Rabinovitz, *Bull. Israel Res. Council* **8A**, 172 (1959).

[11] J. L. Everett and G. A. R. Kon, *J. Chem. Soc.* 1601 (1948).

TABLE 1

Compound	Absorption (in c/s)	Relative intensities, fd.	Assignment of hydrogen atoms	Relative intensities, calc.	Dipole moment
A	437 (m)	4	aromatic	4	0·5 ± 0·1 D
	402 (s)	1	4,5	1	
	311 (s)	1	8	1	
I, R = H	450–418 (m) 414·5 (s)	15	aromatic 4,5	13 2	1·58 ± 0·03 D
	390 (s)	1	8	1	
I, R = Cl	450–400 (m)	12	aromatic	12	2·05 ± 0·03 D
	414·5 (s)	2	4,5	2	
	385·5 (s)	1	8	1	
II[a]	452 (m)	4	aromatic	4	
	421 (s)	1	4,5	1	5·4 D
III	467–427 (m)	12	aromatic in the condensed ring	12	
	422 (s)	5	aromatic in the phenyl group	5	not measured
	394 (s)	1	8	1	
B[a]	490 (m)	1	in *ortho* to carbonyl	1	
	447 (m)	3	other aromatic	3	2·9 D
	414·5 (s)	1	4,5	1	
IV	513 (s)	1	naphthalenic hydrogen, near to carbonyl	1	
	500–487 (m) 470 (m) 459–441 (m)	9	all other aromatic hydrogen atoms including the *ortho* to carbonyl	9	2·88 D
	421 and 411 (q)	2	4,5 (not equivalent)	2	
V	521, 529 (d or m)	2	naphthalenic hydrogen atoms near carbonyl	2	
	482–445 (m)	10	other naphthalenic hydrogen atoms	10	2·88 D
	436·5 (s)	2	4,5	2	
1,1-Diphenylethylene[b]	324		ethylenic		

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[a] D. J. Bertelli, C. Golino and D. L. Dreyer, *J. Amer. Chem. Soc.* **86**, 3329 (1964) found 426 c/p for 8,8-dicyanoheptafulvene and 420 c/s for tropone.

[b] G. V. D. Tiers in *Characteristic NMR Shielding Values* Vol. II, p. 8. Minnesota Mining and Manufacturing Co., St. Paul, Minn. (1958).

Table 1.—(*cont.*)

Compound	Absorption (in c/s)	Relative intensities, fd.	Assignment of hydrogen atoms	Relative intensities, calc	Dipole moment
cis-Stilbene[c]	393		ethylenic		
Tri-phenyl-ethylene	440·5 (s)	10	benzene rings in plane	10	
	427 (s)	5	benzene rings twisted	5	
	421 (s)	1	ethylene	1	
VII	91 (m, no splitting)	1	hydroxyl hydrogen	1	
	209, 216 (d)-1 230, 237, 239, 245-2(hydrogens)	3	aliphatic	1 + 2	
	390 (s)	2	4,5	2	
	417 (s)	8	benzenic	8	
VI	420–448 (m)	7	naphthalenic	7	
	392 (s)	1	ethylenic	1	

[c] *Varian Associates, NMR Spectra Catalog* spectrum 305 (1962).

The same relation follows from the comparison of I (R = H) and triphenylethylene.

Introduction of a chlorine atom in I causes a slight shift in the expected sense, creating a slightly more polar molecule; as the shift is produced by a change in the substituent *near* to H_8, it cannot be employed as an indication of a possible change in aromaticity.

The comparison of I (R = H) and III shows that annelation of a benzene ring at the C_4–C_5 double bond causes a shift of the absorption of H_8 to lower field, i.e., an increase in polarity, and a decrease in aromaticity.

2. *Absorption of* H_4 *and* H_5. The difference between the hydrogen atoms H_4 and H_5 in the dibenzoheptafulvene system and of the hydrogen atoms in *cis*-stilbene or *cis*-1,2-di-(2-naphthyl)-ethylene (VI) is most striking, especially as the hydrogen atoms in these two "open" olefins have the same (393, 392 cps) absorption. The fact that the absorption in (A) is at lower field, as compared with *cis*-stilbene, shows that the conjugation between the benzene rings is greater in the heptafulvene, probably because of the greater spatial constraint imposed by the seven-membered ring.

The comparison of A and I (R = H) shows a shift of the absorption of H_4 and H_5 to lower field for the latter (12·5 c/s). Following the argument presented on page 225, this shift can only be ascribed to an increase in aromaticity on going from A to I (R = H). Introduction of a chlorine atom into the *para*-position of the phenyl ring in C_8 does not cause any change in the absorption of H_4 and H_5. This is particularly significant, as we have seen that this introduction of the chlorine atom influences the H_8 absorption considerably and also increases the dipole moment of the molecule. We see here that the aromaticity cannot be measured by the increase in moment in such a case.

Also the introduction of two cyano-groups (II) into the 8-position of (A) causes a shift of the absorption of H_4 and H_5 to lower field, indicating a higher aromaticity.

The most interesting observations have been made in the series of ketones (B), (IV) and (V). Firstly, the replacement of the terminal methylene group A by oxygen has as strong an influence on the absorption of the hydrogen atoms H_4 and H_5 as the introduction of a phenyl[12] although the concomitant increase in the dipole moment is much higher. Annelation of one benzene ring in the position most remote from C_4–C_5 causes only a slight shift to lower field (6·5 c/s), and only one of the two hydrogen atoms concerned is affected, while the annelation of a second benzene ring leads to a considerable shift, compared with B (22 c/s). In both cases, the dipole moment is unchanged. The discontinuity of the shift to lower field is all the more surprising, as it has no counterpart in the formally analogous pair *cis*-stilbene, *cis*-1,2-di-(2-naphthyl)-ethylene. These observations show again that the dipole moment is not necessarily an indication of the aromatic character of a system such as the one discussed here; changes in the dipole moment only indicate a change in the relative contribution of polar (zwitterionic) forms. This is particularly obvious if one sees that the absorption of H_4 and H_5 is identical in such substances as I and B.

3. It is noteworthy that in VII the hydrogen atoms at C_4 and C_5 absorb at approximately the same field as those in *cis*-stilbene. The system of 2,3,6,7-dibenzocyclohepta-2,4,6-triene in VII is thus entirely different from that system occurring in heptafulvenes.

CONCLUSIONS

The observations reported here show that the system of dibenzoheptafulvene (A) and of dibenzotropone (B) is pseudoaromatic, different from the—formally similar—*cis*-stilbene. The aromaticity of the systems A and B can be measured by the NMR absorption of the hydrogen atoms at the "central" double bond C_4–C_5, their polarity by the absorption of the hydrogen atom at C_8.

The aromaticity of A increases by substitution of the 8-position with aryl or cyano groups, the aromaticity of B by annelation in the positions most remote from the central double bond. In the latter case, the increase occurs in discontinuous jumps.

Aromaticity and polarity of such systems as those studied here need thus not be parallel.

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[12] In 4,5-benzotropone, a value of 415 c/s has been found for the hydrogen atoms of the seven-membered ring. D. J. Bertelli, *J. Org. Chem.* **29**, 3032 (1964).