Tetrahedron. Vol. 24, pp. 6889 to 6896. Pergamon Press 1968. Printed in Great Britain

HMO CORRELATIONS WITH THE ELECTRONIC SPECTRA OF A LARGE NON-HOMOGENEOUS SERIES

A. J. WOHL

Department of Pharmacology, Schering Corporation, Bloomfield, New Jersey

(*Received in USA* 31 *January* 1968; *Received in the UK for publication* 5 *July* 1968)

Abstract—A basic set of electronic spectra for 46 compounds of widely divergent structures have been used to form a correlation with HMO transition energies for *p*-bands, and β-bands. Regression equations have been used to predict the location of these bands in a varied series of 88 additional compounds. The results serve to extend the applicability of the Hückel method as a simple tool for the qualitative and approximate quantitative prediction of the basic elements of singlet transitions.

INTRODUCTION

APPLICATION of the Hückel MO-LCAO (HMO) method to the prediction of the basic features of electronic spectra has met with success within structurally limited families of organic compounds.[1-6] Extension of the HMO technique to divergent structural types or to compounds containing a multiplicity of heteroatoms has been less frequent, and often less successful.[6-10]

One reason for the lack of heteromolecular studies seems to be the difficulty in assignment of bands.[1] These difficulties may be partially overcome by judicious selection of a number of compounds of structural categories sufficiently broad to embrace most varieties of organic compounds whose spectra, reported in non-polar solvents, show acceptable fine structure.

HMO correlations using such a series of prototype compounds may then be employed to predict the location of similar bands in an even wider variety of organic heteromolecules. The present study demonstrates the applicability of the above approach and the general, albeit approximate and empirical utility of the HMO technique in such an application.

RESULTS AND DISCUSSION

The compounds used to obtain "reference" spectra-MO correlations are listed in Table 1. It can be seen that the range of values is comparatively wide for both β-bands and for p-bands. The calculated energy for the β-transition is, in this case, expressed as the average of the second and third excitation energies.[1] The theoretical basis for the averaging technique used to obtain correlations with the higher energy β-bands[1] is distinctly obscure. Configuration interaction will be simulated by this technique when the second and third excitation energies lead to states of similar symmetry, but this is not a frequent occurrence. However this may be, the correlation coefficients obtained for β-bands using second or third excitation energies alone are statistically significantly lower than that reported above as the average of the two.

TABLE 1. BASIC COMPOUND SET FOR PREDICTION

Name and number	Energy of β-transition band		Energy of p-transition band	
	Observed (eV)	Calculated (β_0)	Observed (eV)	Calculated (β_0)
Benzene (1)	6·73	2·0000	6·07	2·0000
Napththalene (2)	5·61	1·6180	4·34	1·2360
Anthracene (3)	4·92	1·4142	3·31	0·8284
Pentacene (4)	4·10	0·7971	2·12	0·5414
Rubicene (5)	4·17	1·0645	2·35	0·6531
Isorubicene (6)	3·91	1·0601	2·20	0·6278
Benzo[a]naphtho[1.8.7-cde]	3·90	0·9994	2·77	0·6828
Dibenzo[h.rst]pentaphene (8)	4·16	1·0754	3·19	0·7914
9,10-Dibromoanthracene (9)	4·73	1·4109	3·05	0·8218
Isoquinoline (10)	5·74	1·6126	4·07	1·2268
Benzo[f]quinoline (11)	4·66	1·3709	4·34	1·1926
Benzo[h]quinoline (12)	4·68	1·3690	4·20	1·1948
Benzo[f]isoquinoline (13)	4·99	1·3681	4·25	1·2097
Benzo[h]isoquinoline (14)	5·05	1·3703	4·20	1·2026
Toluene (15)	6·57	1·9686	5·96	1·9185
Quinoxaline (16)	5·33	1·5990	3·91	1·1981
Quinazoline (17)	5·64	1·6139	3·99	1·2304
Cinnoline (18)	5·58	1·5959	3·85	1·1919
2-Chloroquinoxaline (19)	5·19	1·5910	3·74	1·1989
2-Methoxyquinoxaline (20)	5·08	1·5240	3·68	1·1680
Phenoxazine-3-one (25)	4·66	1·2607	2·87	0·6972
Naphtho[2.1-b]furan	4·53	1·2298	3·73	0·9155
Cyclopenta[c]azepine (27)	4·53	1·2298	3·73	0·9155
Naphtho[2.3-b]carbazole (28)	4·24	1·1110	2·67	0·7077
Hexamethylbenzene (29)	6·12	1·8101	5·61	1·8101
Acridine (30)	4·98	1·4178	3·27	0·8356
Acridinylium cation (31)	4·87	1·4627	3·50	0·9255
1-Hydroxyacridine (32)	4·77	1·3653	3·10	0·8176
1-Hydroxyacridinylium cation (33)	4·55	1·40	3·49	0·8758
3-Hydroxyacridine (34)	4·47	1·3656	3·44	0·8339
4-Hydroxyacridine (35)	4·83	1·3586	3·22	0·8036
9-Aminoacridine (36)	4·77	1·4113	3·05	0·8226
2,6-Diamonoacridine (37)	4·55	1·2343	2·82	0·7435
3-Aminoacridine (38)	4·72	1·2572	3·02	0·8062
Riboflavin† (39)	4·65	1·2366	2·79	0·7863
Benzo[a]acridine (40)	4·50	1·1732	3·23	0·9158
Benzo[b]acridine (41)	4·33	1·0763	2·66	0·5950
Benzo[c]acridine (42)	4·52	1·1690	3·23	0·9001
3,6-Diaminoacridine (43)	4·72	1·1967	3·13	0·8080
4,5-Diaminoacridine (44)	4·61	1·1531	2·91	0·7207
2,3,6,7-Tetrahydroxyanthracene (45)	4·67	1·2905	3·21	0·8172
Phenazine (46)	4·99	1·4028	3·10	0·8056

† Parent structure treated; aliphatic side chain ignored.

While possibly fortuitous, therefore, the averaging technique seems more useful than single Hückel energies for high energy transitions.

$$Y_\beta = 2{\cdot}5550\,\beta_0 + 1{\cdot}4111 \qquad r = 0{\cdot}945 \tag{1}$$

$$Y_p = 2{\cdot}6582\,\beta_0 + 0{\cdot}9062 \qquad r = 0{\cdot}966 \tag{2}$$

Eqns (1) and (2) describe the relationship of the observed β- and p-band energies in eV to the calculated energies using simple HMO techniques. β_0 in these equations refers to the appropriate Hückel transition energy in units of β_0. The high correlations imply that the regression "fits" obtained may be of physical as well as statistical significance. Furthermore, the values obtained for β_0, $-2{\cdot}555$ and $-2{\cdot}658$ eV are well within the range of values obtained by other authors,[1] using more restricted groups of compounds, and close to the usual spectroscopic value for $\beta_0 = -2{\cdot}944$ eV.[11]

Figs. 1 and 2 graphically illustrate these correlations. It is clear that, whereas the estimates are seldom exact, the values obtained are entirely adequate to approximate

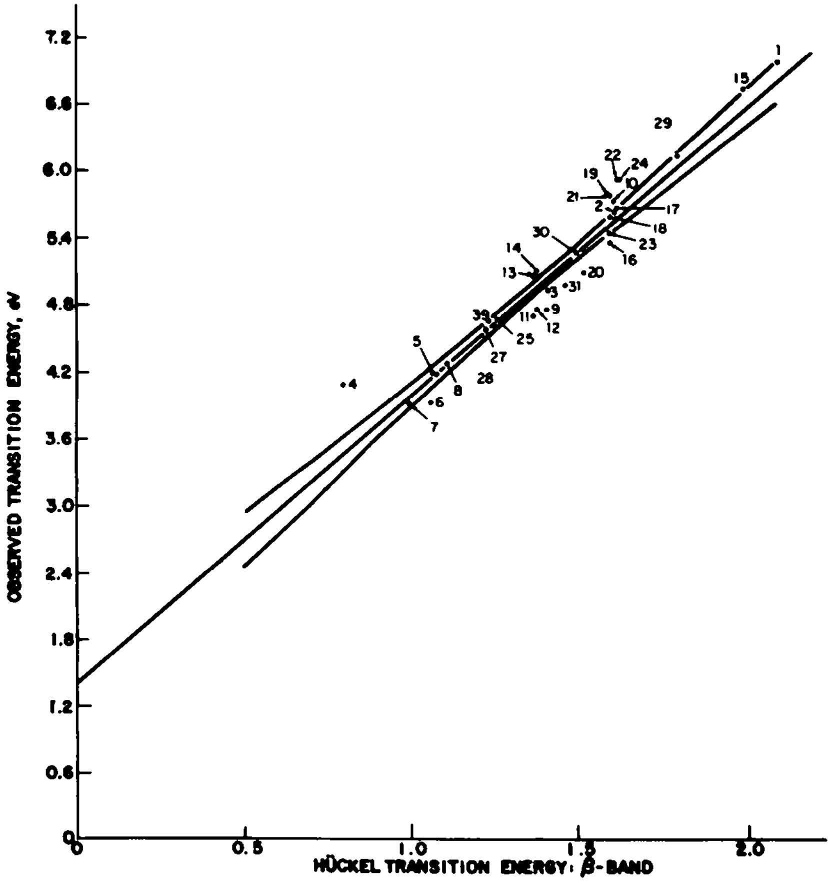

Fig. 1.

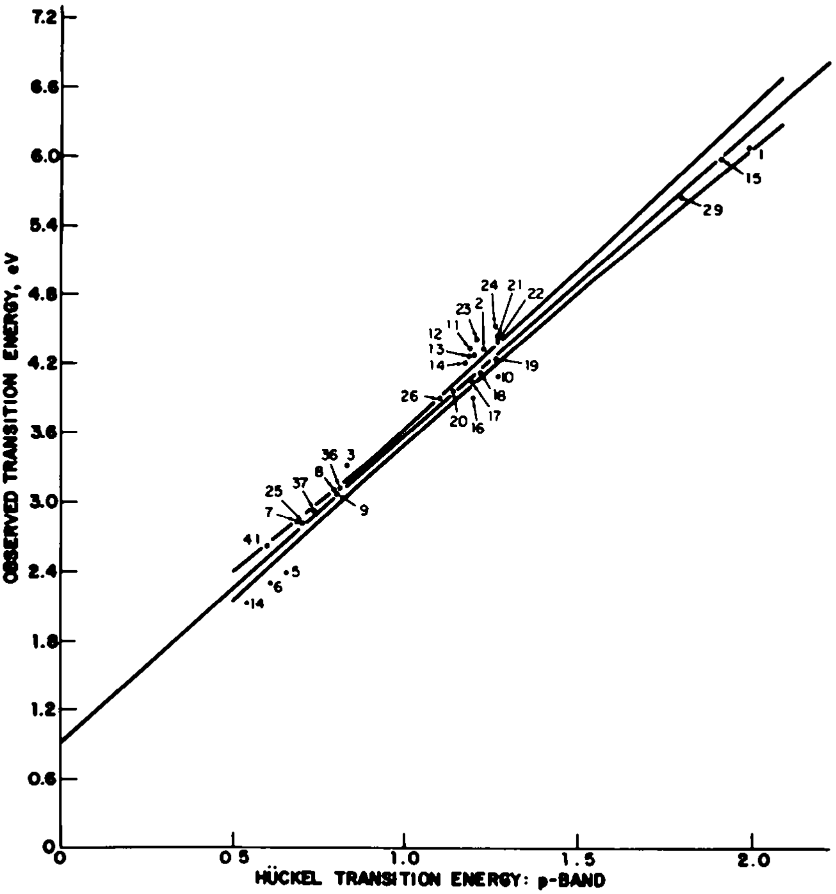

FIG. 2.

correct band positions generally within or close to the boundaries of the 95% regression lines (shown). The numerals on the points plotted in Figs 1 and 2 refer to the compounds in Table 1.

The usefulness of the correlations obtained in this study is remarkable when viewed against the background of the complex variables involved in electronic spectral transitions. Whereas Hückel MO's are adequate to be used as a basis set for trial input to SCF–MO formulations, the precision of the simple HMO technique is dubious in that no distinctions are made between singlet and triplet states, degenerate states, which normally undergo Jahn–Teller distortion, remain degenerate in the HMO method, no provision is made for inclusion either of configuration interaction (except as a fortuitous and limited condition of the analytical technique used above) or of interelectronic repulsions.

TABLE 2. EFFICACY OF HMO BAND PREDICTION

Compound name	β-band β(eV) = $2{\cdot}5550\,\beta_0 + 1{\cdot}4111$ eV		p-band p(eV) = $2{\cdot}6582\,\beta_0 + 0{\cdot}9062$	
	Observed	Predicted	Observed	Predicted
2*H*-Cyclopenta[d]pyridazine	5·08	4·9853	4·01	3·6795
2-Hydroxyphenazine	4·84	4·8552	3·06	3·0157
1,3,4-Trimethyl-2-hydroxyphenazine	4·65	4·7689	3·03	2·8980
1-Hydroxyphenazine	4·73	4·8455	2·95	2·9551
6-Aminoquinoxaline	4·88	5·1332	3·27	3·6370
5-Aminoquinoxaline	4·73	5·2224	3·23	3·5205
9-Vinylacridine	4·92	4·9079	3·22	2·8661
4-Aminoacridine	4·72	4·6332	3·03	2·8722
2-Aminoacridine	4·78	4·6031	3·06	2·9421
4-Mercaptocinnoline	5·60	5·3039	4·09	3·8810
4-Hydroxycinnoline	5·50	5·4628	3·99	4·0224
Phthalimide	5·74	5·4608	4·20	4·3879
Phenothiazine	4·87	5·1427	3·88	3·8557
Benzimidazole	6·16	5·8139	4·96	4·8350
Phenanthridine	5·05	4·9181	4·15	4·1069
2-Aminoquinoline	5·15	5·2423	3·96	4·0216
Fluorenone	4·84	4·8688	3·14	3·2420
2-Methylfluorenone	4·92	4·8389	3·10	3·1604
3-Methylfluorenone	4·77	4·8187	3·29	3·2518
2,7-Dimethylfluorenone	4·71	4·8141	3·02	3·0888
1,4-Benzoquinone-N-phenylimine	4·82	4·8568	2·76	2·7595
Anthraquinone	4·57	4·2190	†	2·2962
1-Aminoanthraquinone	4·58	4·4835	2·62	2·7847
1,4-Dihydroxyanthraquinone	4·43	4·6350	2·59	3·0806
1,4-Diaminoanthraquinone	4·27	4·3425	2·12	2·4254
1,5-Diaminoanthraquinone	4·48	4·1076	2·60	2·7364
o-Naphthoquinone	4·98	4·8537	3·10	3·1279
p-Naphthoquinone	5·04	5·0990	3·73	3·2638
Tetrachloro-*o*-benzoquinone	†	4·6169	4·31	4·4982
Benzo[b]naphtho[2.3-d]thiophene ⊙	4·52	4·8494	3·76	3·8371
9-Xanthone	5·24	5·4748	3·85	4·0458
1,6-Dimethyl-9-xanthone	5·15	5·4076	3·84	4·0580
2,6-Dimethyl-9-xanthone	5·17	5·3685	3·80	3·9884
3,6-Dimethyl-9-xanthone	5·18	5·3951	3·89	4·0966
1*H*-Indazole	†	5·6831	4·81	4·4831
2-Azapyren-1[2*H*]-one	4·82	4·6074	3·29	2·9312
3-Amino-7-oxophenoxazine	4·36	4·4817	2·28	2·6452
2-Aminophenoxazine-3-one	4·55	4·3202	2·48	2·4001
2-Hydroxyphenoxazine-3-one	4·46	4·5216	2·64	2·6877
Phenoxazine	5·18	5·4518	3·93	4·3993
1,5-Naphthyridine	5·20	5·5855	4·65	4·2279
Chalcone	5·44	5·2229	3·96	3·8632
Pentabromoaniline	5·48	5·9590	4·82	5·0971
Styrene ⊙	5·78	5·8407	4·99	4·8068
Isophthalonitrile	5·50	5·4156	5·28	4·7819
Phthalonitrile	5·33	5·3908	5·10	4·4809
Terephthalonitrile	5·05	5·6345	4·60	4·3781
Benzoic acid	6·04[16]	6·1100	5·48	5·2391

Table 2—*continued*

Compound name	β-band $\beta\,(\mathrm{eV}) = 2{\cdot}5550\,\beta_0 + 1{\cdot}4111\,\mathrm{eV}$		p-band $p\,(\mathrm{eV}) = 2{\cdot}6582\,\beta_0 + 0{\cdot}9062$	
	Observed	Predicted	Observed	Predicted
3-Methylbenzoic acid	6·04	6·0236	5·39	5·0450
4-Methylbenzoic acid	6·07	6·0259	5·29	5·1925
Dibenzo[a.h]acridine	4·20	3·7384	3·14	2·4884
Dibenzo[c.h]acridine	4·10	3·8884	3·32	2·7752
Dibenzo[a.j]acridine	4·24	4·2420	3·31	3·5322
Dibenzo[a.i]carbazole	4·47	4·4508	3·39	3·8709
Octaethylporphin	3·11	3·2502	2·35	2·3483
Quinoline	5·49	5·5402	4·14	4·1819
5,10,14c-Triazabenzo[a]naphth-[1.2.3-de]anthracene	4·07	4·0872	2·83	3·0027
9,10,15,15b-Tetraazanaphtho-[1.2.3-fg]naphthacene	3·96	3·8023	2·45	2·5165
9-Benzylidenefluorene	4·81	4·5468	†	3·3685

† Spectra unavailable in this region.

⊙ Orbital degeneracy present.

A planar, especially a cyclic and planar molecule existing in a unique rigid conformation, however, has the gross features of its electronic spectrum primarily determined by the comparatively crudest features of its geometry such as interatomic distances.[1] For such molecules, by far the majority of compounds treated in this or other studies, it would seem that Hückel orbitals account rather well for singlet transitions with a scaling factor equal to β_0.

The predictive value of the correlations of equations (1) and (2), was tested with a selection of 88 additional compounds. The compounds so studied as well as observed values and predicted values for spectral transition energies are tabulated in Table 2.

Our results indicate that, on the average, it is possible to predict band locations within ±6 mμ (0·18 eV) for β-bands, and within ±7 mμ (0·21 eV) for p-bands.

It would be informative if the results of the present study could be compared with results of other workers. Unfortunately, while a number of highly successful studies have been published correlating HMO results with the electronic spectra of a variety of related hydrocarbons, practically no work along these lines deals with molecules containing multiple heteroatoms. One exception,[19] deals with a small series of mesoionic sydnones. This study found a deviation of ±7 mμ from the straight line plot using the omega technique. The studies on hydrocarbons,[2,4,5] show comparable deviations.

It should be clear that, while the HMO technique is shown by the present study to be applicable to a very diverse group of organic chemicals as a predictor of the gross elements of electronic spectra, no overriding emphasis is to be placed on the surprisingly good predictability of the technique. The present work simply supports the utility of the HMO approach as a simple tool for results of generally adequate precision.

METHODOLOGY

Hückel calculations replace the formal inclusion of interelectronic repulsions and core Hamiltonians in the SCF method with empirical values for Coulombic and resonance integrals.[1] Such empirical values are expressed as functions of α_0 and β_0, respectively, the Coulomb integral and the resonance integral of an sp^2 carbon in benzene for an aromatic C—C bond of about 1·4 Å length. The functions are given as:

$$\alpha_x = \alpha_0 + h_x\beta_0$$

$$\beta_{cx} = k_{cx}\beta_0$$

where h and k are empirically determined parameters of the atom and bond, respectively. Table 4 gives the values used in the present study.

TABLE 3. HMO PARAMETERS FOR COULOMB AND RESONANCE INTEGRALS

$\alpha_x = \alpha_0 + h_x\beta_0$			$\beta_{xy} = k_{xy}\beta_0$		
Element	h	Typical molecule	Bond	k	Typical molecule
C	0	Benzene	C═C	1·0	Benzene
C	0·1	Acetylene	C≡C	1·4	Acetylene
N·	0·4	Pyridine	C═C	1·1	Ethylene
N:	1·0	Aniline	C—C	0·9	Butadiene
N^+	2·0	Phenyltrimethylammonium	C—C	0·7	Toluene
O·	1·2	Benzaldehyde	C—F	0·7	Halobenzenes
O:	1·4	Anisole	C—Cl	0·4	
O:	2·0	Furan	C—Br	0·3	
F	3·0	Fluorobenzene	C—I	0·2	
Cl	2·0	Chlorobenzene	C═N	1·0	Pyridine
Br	1·5	Bromobenzene	C—N	0·8	Aniline
I	0·8	Iodobenzene	$C—N^+$	0·7	Phenyltrimethylammonium
S†	0	Thiophene	C≡N	1·5	Benzonitrile
C_α	—0·1	Toluene: C_α—CH_3	C—CN	0·9	Benzonitrile
C	−0·2	Toluene	C—O	0·8	Phenol
$\equiv H_3$	−0·5	Toluene	C═O	1·2	Benzaldehyde
			C—S†	0·5	Thiophenol
			N═N	1·0	Cinnoline
			$C\equiv H_3$	2·5	Toluene
			S′—S″†	1·0	Thiophene

† Divalent sulfur was treated, as in other studies, assuming pd-hybridization.[11,12]

Solutions of the Hückel matrices, ignoring overlap, were performed by digital computer. The energy levels, in units of β_0, are shown for the calculation performed on acridine (Table 4). The lowest energy $\pi \rightarrow \pi^*$ transition, symbolized by a one-electron jump from the occupied orbital of highest energy, numbered 0, to the unoccupied orbital of lowest energy, numbered -1, is assumed to represent the p-band.[1,11]

Similarly, a one-electron jump from the penultimate occupied orbital to the lowest empty orbital ($1 \rightarrow -1$) is assumed to represent the β-band.[1,20] Although the compounds studied were not all hydrocarbons, Clar's[20] symbolism is used throughout.

TABLE 4. π-ELECTRON ENERGY LEVELS (IN UNITS OF β_0) FOR ACRIDINE

Energy levels		
2·3830		
2·0000		
1·4142		
1·3386		
1·0000		
0·3417		
0·3417	−1†	
−0·4939	0	Occupied molecular orbitals
−1·0000	1	
−1·0000		
−1·4142		
−1·5103		
−2·0000		
−2·4590		

† For numeration see text.

The electronic spectra used in this study are taken from *UV Atlas of Organic Compounds*, Vols. I, II, Plenum Press, New York, 1966, except where otherwise noted.

Standard computational routines for linear correlation and regression were used to obtain the reported correlation coefficients and regression equations.

Acknowledgement—The assistance of the Department of Statistics and Scientific Programming, Schering Corporation is gratefully acknowledged.

REFERENCES

[1] A. Streitweiser, Jr., *Molecular Orbital Theory for Organic Chemists*. Wiley, New York (1961).
[2] R. Zahradnik, C. Parkanyi, J. Michl and V. Horak, *Tetrahedron* **22**, 1341 (1966).
[3] S. F. Mason, *Ibid.* **19** (Suppl. 2), 265 (1963).
[4] R. Zahradnik, J. Michl, and J. Mancir, *Ibid.* **22**, 1355 (1966).
[5] J. Michl, R. Zahradnik, and P. Hochmann, *J. Phys. Chem.* **70**, 1732 (1966).
[6] T. E. Peacock, *Electronic Properties of Aromatic and Heterocyclic Molecules*. Academic Press, New York (1965).
[7] F. A. Matsen, *J. Am. Chem. Soc.* **72**, 5243 (1950).
[8] A. K. Chandra and S. Basu, *J. Chem. Soc.* 1959 (1623).
[9] H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.* **18**, 1174 (1950).
[10] B. Pullman, A. Pullman, G. Berthier, and J. Pontis, *Bull. Soc. Chim. Fr.* **18**, 271 (1952).
[11] H. C. Longuet-Higgins, *Trans. Farad. Soc.* **45**, 173 (1949).
[12] M. K. Orloff and D. D. Fitts, *Biochim. Biophys. Acta* **47**, 596 (1961).
[13] E. D. Bergmann, E. Fischer, and J. H. Jaffe, *J. Am. Chem. Soc.* **75**, 3230 (1953).
[14] E. A. Steck and G. W. Ewing, *Ibid.* **70**, 3397 (1948).
[15] American Petroleum Institute Research Project No. 441, 1947. Shell Development Co.
[16] J. W. Baker, G. F. C. Barrett, and W. T. Tweed, *J. Chem. Soc.* 2831 (1952).
[17] C. M. Moser and A. I. Sohlenberg, *Ibid.* 804 (1951).
[18] J. R. Platt, *J. Chem. Phys.* **18**, 1168 (1950).
[19] L. B. Kier and E. B. Roche, *J. Pharm. Sci.* **55**, 807 (1966).
[20] E. Clar, *Aromatische Kohlenwasserstoffe* (2nd Edition) Springer-Verlag, Berlin (1952).