EXPERIMENTAL AND THEORETICAL (HMO AND LCI-SCF) STUDY OF SINGLET-TRIPLET TRANSITIONS IN CONJUGATED HYDROCARBONS AND THEIR DERIVATIVES

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Experimental wavenumbers of maxima of absorption and emission (phosphorescence) bands are found to be linearly correlated with the HMO N → V_1 transition energies[1]. The correlations are close enough to be used to estimate energies of the first triplet state of the compounds, for which no experimental data are available. LCI–SCF (PPP) parameters are given which permit these energies to be calculated with satisfactory accuracy.

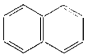
The extraordinary importance of the first triplet state, in particular in photochemistry, is generally recognized. Nevertheless and despite the fact that both HMO[1] and SCF[2] calculations give good energy values for S–S transitions[3], quantum chemical estimations of S – T transition energies have been unsatisfactory until recently.

The energy of the first excited triplet state with respect to the singlet ground state can be determined from absorption and emission (phosphorescence) measurements. Both these measurements should be used in conjunction for a reliable determination of the 0 → 0 vibrational transition. Although S — T transitions are strongly spin forbidden, they can become weakly allowed through the influence of paramagnetic species such as O_2[4] and NO[5] in solution or by introducing a heavy atom either into the molecule or the solvent (internal or external[6] heavy atom effect).

Soon after finding that the HMO N → V_1 transition energies can be correlated with the wavenumbers of the first intense bands[1] of the singlet-singlet spectra, we attempted a similar correlation of the phosphorescence data for a series of conjugated hydrocarbons. The failure of this attempt is hard to explain (see, however[7]), inasmuch as the lowest HMO excitation energies represent, owing to the approximate nature of the HMO method, an "average" between the $S_0 - S_1$ and $S_0 - T_1$ transitions. Only recently we found the reason for this "failure"; incorrect values in published phosphorescence data[8].

EXPERIMENTAL AND CALCULATIONS

Compounds studied. Compounds investigated are listed in Appendix. For sixteen of them the S — T absorption measurements were carried out. Experimental data on the other substances were taken from literature (see Appendix).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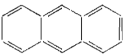
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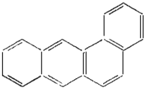
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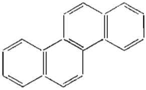
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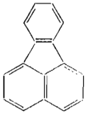
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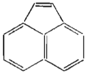
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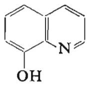
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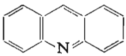
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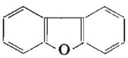
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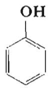
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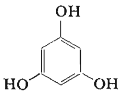
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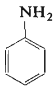
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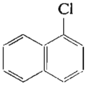
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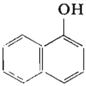
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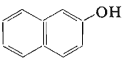
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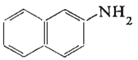
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Absorption measurements. As the molar extinction coefficients of S — T bands range in value from 10^{-3} to 0, the substances must be purified with an extraordinary care. Solid compounds were purified by several crystallizations (the first with carborafin), sublimation and zone melting. These operations were repeated usually 4 or 5 times, until no further changes in melting point and S_0 — S_x absorption curve were observed. Phenol was purified by repeated distillation.

Heavy-atom solvents, methyl iodide and ethyl iodide, were purified by repeated fractional distillation at atmospheric pressure (b.p. 41°C and 71°C, respectively) in the dark, stabilized by a silver wire and stored in a refrigerator. Before use they were passed through an alumina column.

Measurements were made with Unicam SP 700 and Optica Milano CF 4 spectrophotometers in cells of 5 or 10 cm optical path. In most cases 1M solutions were used.

Calculations. HMO calculations were performed with standard parameters adopted in our Laboratory (Table I).

LCI—SCF calculations were performed by our usual[9] procedure. Electronic repulsion integrals were evaluated according to Mataga and Nishimoto[10]; semiempirical parameters used are

TABLE I

Parameters for HMO Calculations

$\alpha_X = \alpha + \delta_X \beta$, $\beta_{CX} = \varrho_{CX} \beta$, where α and β denote the Coulomb and resonance integrals of $2p_z$ carbon orbitals respectively; X stands for a heteroatom.

X	δ_X	C—X	ϱ_{CX}
N(=$\overline{\text{N}}$—)	0·5	C=N	1·0
N(—NH$_2$)	1·0	C—N	0·8
O(=O$\rangle$)	1·0	C=O	1·0
O(—OH)	2·0	C—O	0·8
S(—$\underline{\overline{\text{S}}}$—)	1·0	C—S	0·7
Cl(—$\underline{\overline{\text{Cl}}}$|)	2·0	C—Cl	0·4
Br(—$\underline{\overline{\text{Br}}}$|)	1·5	C—Br	0·3
F(—$\underline{\overline{\text{F}}}$|)	3·0	C—F	0·7

TABLE II

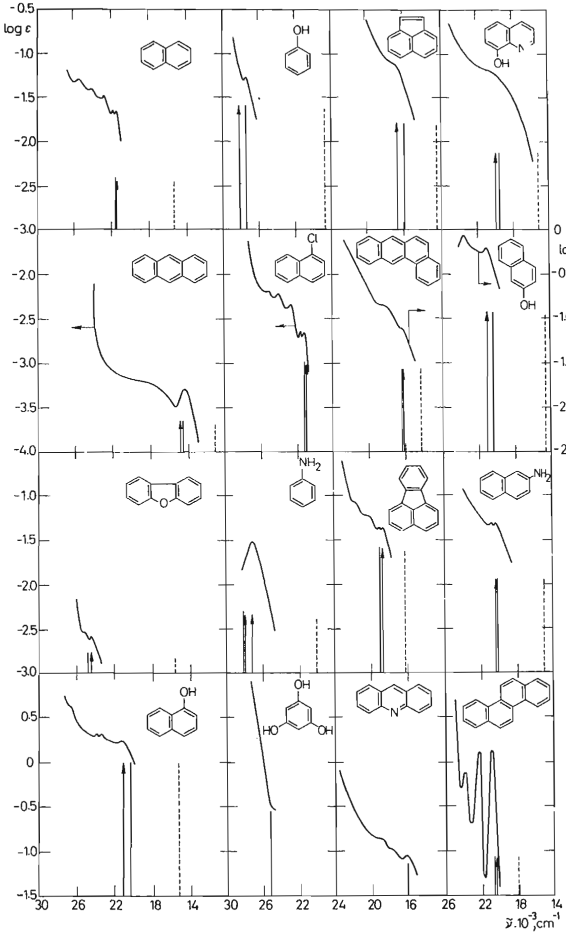
Parameters of the LCI-SCF Method

Data in the upper part of the Table represent a set particularly suitable for calculations of S—T transitions; parameters in the lower part are suitable for calculations of S—S transitions[3]

Group	I_X, eV[a]	A_X, eV	γ_{XX}, eV	β_{CX}/β_{CC}	Z	l_{CX}, Å
—C=	8·80	0·60	8·20	1·00	1	1·40
—OH	30·48	10·02	20·46	1·00	2	1·36
—NH$_2$	24·88	9·32	15·56	0·80	2	1·40
=N—	11·66	2·21	9·45	1·14	1	1·40
—Cl	23·87	13·90	9·97	0·40	2	1·70
			$\beta_{CC} = -2·50$ eV			
—C=	11·22	0·69	10·53	1·00	1	1·40
—OH	32·90	10·00	22·90	1·00	2	1·40
—NH$_2$	27·30	9·30	18·00	0·80	2	1·40
=N—	14·10	1·80	12·30	1·00	1	1·40
—Cl	25·07	13·80	11·27	0·40	2	1·70
			$\beta_{CC} = -2·318$ eV			

[a] Meaning of symbols used in the heading: I_X valence state ionization potential; A_X valence state electron affinity; γ_{XX} one-centre repulsion integral; β_{CX}/β_{CC} relative value of resonance integral; Z core charge; l_{CX} carbon–heteroatom bond length; β_{CC} resonance integral for a C—C bond.

summarized in Table II. The lower part of the table contains values used successfully in calculations of S — S absorption spectra, while the values in the upper part have been employed recently[11,12] in interpreting the maxima of S — T bands.



RESULTS AND DISCUSSION

S – T absorption curves recorded by us are presented in Fig. 1. Wavenumbers of absorption maxima together with data reported by other authors are summarized in the Appendix.

A plot of wavenumbers of S – T absorption maxima against the HMO N → V_1 transition energies is seen, in Fig. 2, to represent a single simple correlation. The same correlation for S – T emission maxima is presented in Fig. 3. Its splitting by structural type, which is common in HMO correlations[3], does not occur.

It should be mentioned that the HMO excitation energies were obtained with standard parameters, *i.e.* without a parametrization study. Furthermore the experimental data were obtained from various sources. In view of the fair correlation found most of the experimental data appear therefore to be reasonably reliable.

For estimations of the first excited triplet state with the aid of HMO N → V_1 transition energies we suggest the following relationships.

Absorption data

$$\tilde{\nu}_{\text{exp}}^{\text{S}-\text{T}_1}(10^{-3}\,\text{cm}^{-1}) = 11{\cdot}576E(\text{N} \rightarrow \text{V}_1)\,(\beta) + 6{\cdot}711\,, \qquad (1)$$

$$n = 57 \quad \sigma = \pm\ 1{\cdot}28\,.\,10^3\,\text{cm}^{-1}\,,$$

Emission data

$$\tilde{\nu}_{\text{exp}}^{\text{phosph.}}(10^{-3}\,\text{cm}^{-1}) = 12{\cdot}889E(\text{N} \rightarrow \text{V}_1)\,(\beta) + 5{\cdot}511\,, \qquad (2)$$

$$n = 73 \quad \sigma = \pm\ 1{\cdot}11\,.\,10^3\,\text{cm}^{-1}\,.$$

With the absorption data, a parabolic interpolation appears to be somewhat more accurate[8], particularly with extreme values of N → V_1 energies.

$$\tilde{\nu}_{\text{exp}}^{\text{S}-\text{T}_1} = -\ 5{\cdot}363[E(\text{N} \rightarrow \text{V}_1)]^2 + 26{\cdot}474E(\text{N} \rightarrow \text{V}_1) - 2{\cdot}815\,, \qquad (3)$$

$$n = 57 \quad \sigma \pm\ 1{\cdot}02\,.\,10^3\,\text{cm}^{-1}\,.$$

It is not apparent why the HMO correlations are split according to structural type in the singlet but not the triplet case. It is also puzzling that the triplet data correlate much worse with LCI-SCF than with HMO calculations. It should of course be

FIG. 1

S – T Absorption Curves of Conjugated Compounds in Ethyl Iodide

Arrows indicate 0 – 0 maxima of phosphorescence bands (reported data), full and dashed lines represent LCI – SCF energies of S_0 – T_1 transitions calculated with the aid of old and new parameters, respectively. Figures are arranged according to wavenumber region in which absorption curve occurs.

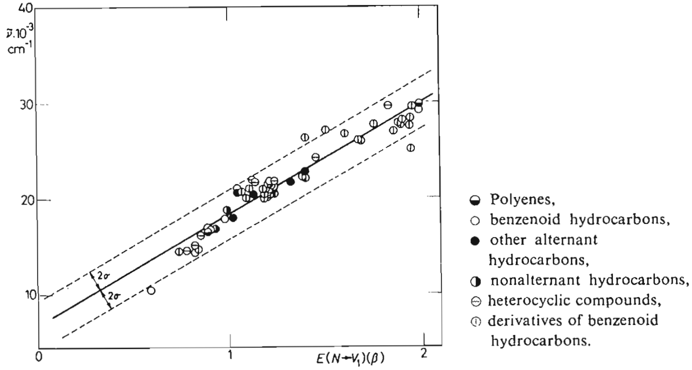


FIG. 2

Plot of Wavenumbers of the First Absorption Maxima of S – T Bands *vs.* HMO N → V_1 Transition Energies (for numerical data and designation see Appendix)

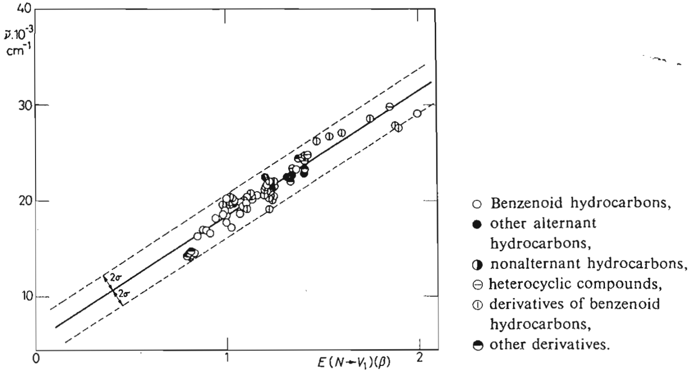


FIG. 3

Plot of Wavenumbers of the First Maxima of Phosphorescence Bands *vs.* HMO N → V_1 Transition Energies (for numerical data and designation see Appendix) realized that the S – T transition energies were calculated with the aid of parameters suitable for the study of S – S transitions. It appears the nature of $S_0 - T_1$ transitions differs from that of $S_0 - S_1$ transitions, where on passing to LCI-SCF excitation

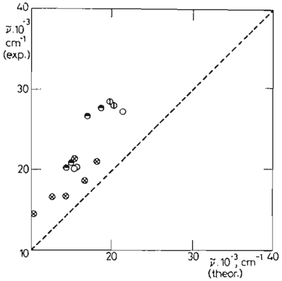


FIG. 4

Plot of Experimentally Found Wavenumbers of the First Absorption Maxima of S – T Bands *vs.* Calculated LCI–SCF Transition Energies (parametrization suitable for S – S transitions)

◓ Hydroxy derivatives, ○ amino derivatives, ⦶ chloro derivatives, ⊗ unsubstituted benzenoid hydrocarbons.

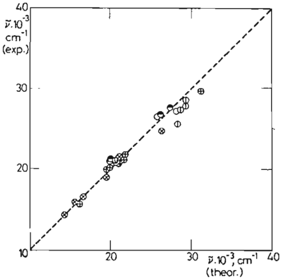


FIG. 5

Plot of Experimentally Found Wavenumbers of the First Absorption Maxima of S – T Bands *vs.* Calculated LCI–SCF Transition Energies (parametrization suitable for S – T and T – T transitions)

◓ Hydroxy derivatives, ○ amino derivatives, ⦶ chloro derivatives, ⊕ aza analogues of benzenoid hydrocarbons, ⊗ unsubstituted benzenoid hydrocarbons.

energies a split in the correlation disappears[1] and the data corresponding to various structural types fall on one line having a unit slope.

It is possible to overcome the difficulty of the LCI-SCF method with S – T transitions: with changed parameters, agreement is satisfactory for S – T and T – T transitions (compare Table II, upper part)[8,11]. However, this modified set of para-

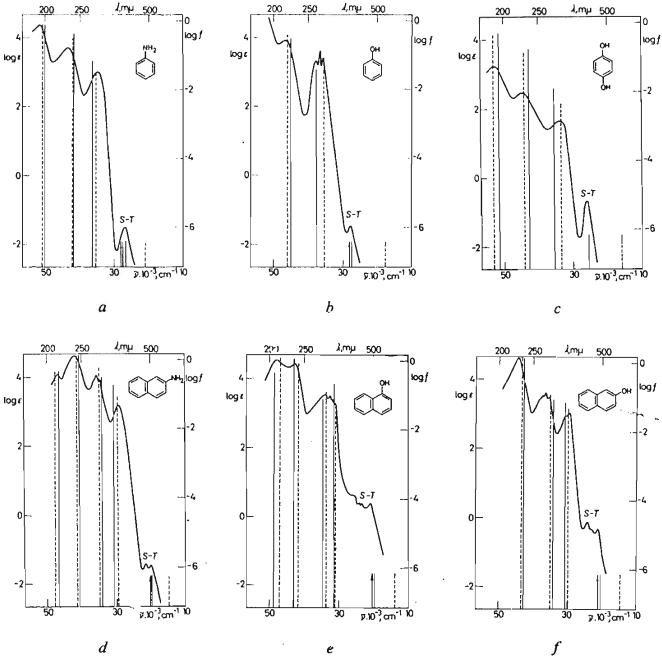


FIG. 6

S — S and S — T Absorption Curves of Aniline (*a*), Phenol (*b*), Hydroquinone (*c*), β-Naphthyl Amine (*d*), α-Naphthol (*e*), β-Naphthol (*f*) in n-Hexane (S — S) and Ethyl Iodide (S — T)

LCI—SCF excitation energies and logarithms of oscillator strengths are calculated by means of parameters presented in the upper (——) and lower (— — —) part of Table II. Wavenumbers of S — T transitions are indicated by short lines (again ——— and — — —). 0—0 maxima of phosphorescence bands are indicated by arrows.

meters cannot be adopted for the general interpretation of S − S transitions. A possible but unproved explanation for this difficulty appears to be a different correlation energy in singlet and triplet states, which is taken into account in semiempirical calculations only through the values of parameters.

Experimentally found energies of the first triplet states are seen, from Fig. 5, to be linearly dependent on the LCI-SCF excitation energies calculated with the aid of parameters which have been suggested recently[8,11] for calculations of S − T and T − T transition energies. Fig. 5 also presents data for several derivatives of benzenoid hydrocarbons. For the determination of semiempirical parameters for heteroatoms, a study showed that the usual parameters for heteroatoms must be changed like those for the carbon atom; *i.e.*, lower values of ionization potentials and accordingly of one-centre repulsion integrals should be used and higher values of resonance integrals (compare Table II). From Figs 6*a* − 6*f* it can be seen that S − T and T − T parametrization also satisfactorily interprets S − S transitions with the six derivatives studied. However these parameters give an incorrect order of α and *p*-bands for benzenoid hydrocarbons (in Clar nomenclature)[12,13].

APPENDIX

Wavenumbers (10^{-3} cm^{-1}) of the 0−0 Maxima of Absorption and Emission Singlet-Triplet Bands and the Values of $E(\mathrm{N} \rightarrow \mathrm{V}_1)$ Transition Energies (in β-units)

No	Compound	Emission	Absorption	$E(\mathrm{N} \rightarrow \mathrm{V}_1)$
		Polyenes		
1	ethylene	25·00[33,a]	29·80[14], 28·70[15]	2·000
2	butadiene	—	20·75[15], 20·90[16]	1·236
3	*trans*-hexatriene	—	16·45[15]	0·890
4	vitamin A	19·95[34,a,b]	—	0·569
		Benzenoid hydrocarbons		
5	benzene	29·80[33], 29·40[6,36], 29·47[35], 29·00[26], 29·44[37 38]	29·44[17], 29·51[4], 29·67[18], 29·66[18]	2·000
6	naphthalene	21·30[33,39], 21·07[40], 21·25[35], 22·00[26], 21·24[41]	21·18[4], 21·30[19], 21·70[20], 21·40[21,23]	1·236
7	anthracene	14·93[22,35], 14·70[42]	14·85[22], 14·87[4], 14·40[23], 14·80[24]	0·828
8	phenanthrene	21·38[43], 21·60[26], 21·64[44]	21·60[4]	1·210
9	naphthacene	19·60[26,35,a,b]	10·25[25]	0·590

APPENDIX

(*Continued*)

No	Compound	Emission	Absorption	$E(\mathrm{N} \rightarrow \mathrm{V}_1)$
10	benz(*a*)anthracene	18·63^{45}, 16·52^{44}, 16·50^{26}	16·52^{23}	0·905
11	chrysene	20·00^{33,44}, 19·66^{40}, 20·04^{26}	21·00^{23}, 20·00^{21}	1·040
12	benzo(*c*)phenanthrene	20·02^{44}	—	1·135
13	triphenylene	23·25^{44}	—	1·368
14	pyrene	16·94^{45}, 16·80^{26}, 16·85^{44}	16·93^{4}	0·890
15	pentaphene	16·93^{44}	—	0·874
16	dibenz(*a,c*)anthracene	17·77^{44}	17·79^{4}	0·998
17	dibenz(*a,h*)anthracene	19·61^{45}, 18·30^{26}, 18·26^{44}	—	0·947
18	dibenz(*a,j*)anthracene	18·50^{44}	—	0·983
19	picene	20·08^{44}	—	1·004
20	dibenzo(*a,g*)phenanthrene	19·76^{44}	—	1·100
21	dibenzo(*c,g*)phenanthrene	19·80^{44}	—	1·071
22	dibenzo(*a,l*)phenanthrene	18·65^{44}	—	1·064
23	1,2-benzpyrene	18·51^{44}	—	0·994
24	tetrabenzo(*a,c,f,h*)naphthalene	17·27^{44}	—	1·023
25	3,4,6,7-dibenzpyrene	16·36^{45}	—	0·843
26	1,2,6,7-dibenzpyrene	20·36^{44,a,b}	—	1·110
27	tetrabenz(*a,c,h,j*)anthracene	20·55^{44}	—	1·155
28	coronene	19·04^{44}, 18·86^{46}	—	1·078
		Other alternant hydrocarbons		
29	biphenylene	26·50^{47,a}	—	0·890
30	biphenyl	22·80^{33,50}, 22·95^{48}, 22·85^{49}, 22·93^{51}, 22·90^{27}	—	1·409
31	*o*-terphenyl	21·55^{27}, 20·57^{44}	—	1·221
32	*m*-terphenyl	22·50^{27}, 22·60^{49}	—	1·324
33	*p*-terphenyl	22·40^{27}, 20·57^{44}	—	1·185
34	2,2′-dinaphthyl	19·56^{44}	—	1·041
35	1,3,5-triphenylbenzene	22·60^{49}, 22·62^{44}, 22·50^{27}	—	1·324
36	1-phenylnaphthalene	—	20·60^{27}	1·045
37	2-phenylnaphthalene	—	20·53^{27}	1·130
38	styrene	—	21·60^{4,17}	1·324
39	*cis*-stilbene	21·70^{33,a,c}	25·20^{28}	1·001
40	*trans*-stilbene	—	17·75^{4}	1·001

APPENDIX
(*Continued*)

No	Compound	Emission	Absorption	$E(N \rightarrow V_1)$
		Non-alternant hydrocarbons		
41	fluoranthene	18·51[44]	18·45[4], 18·70[23]	0·989
42	acenaphthylene	—	16·40[29], 16·70[23]	0·922
		Heterocyclic compounds		
43	pyridine	30·00[52]	29·65[17]	1·841
44	*s*-triazine	26·40[49,a,d]	—	2·062
45	quinoline	21·70[33]	21·85[17], 21·84[17]	1·230
46	isoquinoline	—	21·21[17]	1·220
47	8-hydroxyquinoline	—	20·00[23]	1·208
48	1-azaanthracene	—	15·07[17]	0·823
49	2-azaanthracene	—	14·87[17]	0·774
50	acridine	—	15·84[4,17], 16·20[23]	0·849
51	1-azaphenanthrene	—	21·88[17]	1·184
52	4-azaphenanthrene	—	21·74[17]	1·187
53	2,2′-dipyridyl	23·42[54]	—	1·350
54	4,4′-dipyridyl	24·86[54]	—	1·412
55	2-phenyl-*s*-triazine	24·50[49]	—	1·420
56	2,4-diphenyl-*s*-triazine	24·40[49]	—	1·348
57	2,4,6-triphenyl-*s*-triazine	24·60[49]	—	1·348
58	dibenzofuran	—	24·30[23]	1·466
		Derivatives of benzenoid hydrocarbons		
59	chlorobenzene	—	28·57[17]	1·950
60	fluorobenzene	—	29·50[4,17]	1·925
61	1,4-dichlorobenzene	27·85[27]	28·05[27]	1·904
62	1-bromo-4-chlorobenzene	—	27·85[27]	1·903
63	1,4-dibromobenzene	27·91[27]	27·80[27]	1·902
64	1,3,5-trifluorobenzene	—	25·15[17]	1·953
65	1,3,5-trichlorobenzene	—	27·68[27]	1·955
66	1,2,4,5-tetrachlorobenzene	—	26·80[27]	1·864
67	phenol	28·50[33,39], 28·60[39]	27·60[23]	1·755
68	catechol	—	none[23,e]	—
69	resorcinol	—	none[23,e]	—
70	hydroquinone	—	26·00[23]	1·692
71	phloroglucinol	—	none[23,e]	—
72	aniline	26·80[33], 27·34[49]	27·20[23]	1·504
73	benzoic acid	27·20[33,39]	—	1·479
74	benzoyl chloride	—	26·28[17]	1·411

APPENDIX

(*Continued*)

No	Compound	Emission	Absorption	$E(N \rightarrow V_1)$
75	benzonitrile	27·00^{33}	26·88^{17}	1·607
76	1-fluoronaphthalene	21·06^{41}	21·00^{30}	1·223
77	2-fluoronaphthalene	21·27^{41}	—	1·230
78	1-chloronaphthalene	20·70^{33}, 20·65^{40,41}	20·44^{27}, 20·65^{30}, 20·50^{23}	1·226
79	2-chloronaphthalene	21·0^{33}, 21·07^{41}	21·05^{27}, 21·30^{23}	1·232
80	1-bromonaphthalene	20·70^{30,33}, 22·72^{31}	20·83^{27}, 20·70^{30}, 20·65^{4}	1·226
81	2-bromonaphthalene	21·040^{27,33}, 21·10^{41}	—	1·232
82	1-Iodonaphthalene	19·00^{39} 20·65^{27,}	18·90^{30}	1·226
83	2-Iodonaphthalene	21·04^{33}, 20·90^{58}, 21·05^{27}	21·00^{32}	1·232
84	1,4-dibromonaphthalene	20·30^{27}	—	1·215
85	1,5-dibromonaphthalene	20·09^{41}	—	1·216
86	2,6-dibromonaphthalene	20·80^{41}	—	1·227
87	1-methylnaphthalene	21·20^{33}, 20·85^{39}	—	1·219
88	2-methylnaphthalene	20·80^{33}	21·30^{27}	1·228
89	1-naphthol	20·50^{33}	21·20^{23}	1·181
90	2-naphthol	21·10^{33}	21·00^{23}	1·196
91	1,5-dihydroxinaphthalene	20·15^{27}	—	1·075
92	2-ethoxinaphthalene	21·64^{27,a}	—	1·031
93	1-naphthylamine	20·10^{33,39}	—	1·080
94	2-naphthylamine	20·10^{33}	20·80^{23}	1·081
95	1,8-diaminonaphthalene	19·10^{33}	—	1·116
96	1-naphthaldehyde	19·90^{33}	—	0·969
97	2-naphthaldehyde	20·40^{56,27}	—	0·986
98	1-naphthoic acid	20·20^{33}	—	1·026
99	1-naphthonitrile	20·10^{33}, 20·90^{39}	—	1·104
100	2-naphthonitrile	20·70^{33}	—	1·163
		Other derivatives of alternant hydrocarbons		
101	1-chloroanthracene	14·73^{22}	—	0·825
102	1,5-dichloroanthracene	14·59^{22}	—	0·822
103	1,10-dichloroanthracene	14·62^{22}	—	0·819
104	9,10-dichloroanthracene	14·15^{22}	—	0·815
105	9,10-dibromoanthracene	14·06^{22}	—	0·815
106	9-methylanthracene	—	14·46^{4}	0·824
107	9-nitroanthracene	—	14·63^{4}	0·711
108	anthraquinone	21·90^{57}	—	1·092
109	2-methylanthraquinone	21·96^{57}	—	0·315
110	5,12-naphthacenequinone	19·65^{25,a,b}	—	0·705

APPENDIX

(*Continued*)

No	Compound	Emission	Absorption	$E(N \rightarrow V_1)$
111	2-bromobiphenyl	$22{\cdot}72^{27,a,c}$	—	1·402
112	2-iodobiphenyl	$22{\cdot}00^{27,a,c}$	—	1·402
113	2,2′-difluorobiphenyl	$24{\cdot}40^{33}$	—	1·387
114	4,4′-difluorobiphenyl	$23{\cdot}00^{33}$	—	1·405
115	2,2′-dichlorobiphenyl	$25{\cdot}00^{33,a,c}$	—	1·396
116	4,4′-dichlorobiphenyl	$22{\cdot}00^{27}$	—	1·396
117	2,2′,4,4′,6,6′-hexachlorobiphenyl	$24{\cdot}50^{33,a,c}$	—	0·715
118	2-nitrobiphenyl	$20{\cdot}80^{33,a,c}$	—	0·401

[a] This value was not used in the calculation of constants of the regression line. [b] This value can probably be assigned to the emission from a higher triplet state. [c] Considerable steric hindrance to coplanarity. [d] n-π^* transition. [e] Experimental attempts to measure the S — T absorption failed.

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