

Crystallographic Studies and Physicochemical Properties of π -Electron Compounds.

III. Stabilization Energy and the Kekulé Structure Contributions Derived from Experimental Bond Lengths

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(Received 13 September 1982; accepted 25 April 1983)

Abstract

Simple-harmonic-oscillator calculations of the deformation energy necessary to transform molecules with π -electron systems into their Kekulé structures are presented. They enable estimation of (i) relative stabilization energies and (ii) Kekulé-structure contributions; both are calculated directly from experimental molecular geometries. Correlation between HOSE (Harmonic Oscillator Stabilization Energy) values and the Hess & Schaad resonance energies for alternant unsaturated hydrocarbons is very good ($r = 0.991$, $n = 22$); for non-alternant species the correlation is worse ($r = 0.937$, $n = 12$) but still acceptable. A very good correlation exists too between percentage contributions of the Kekulé structures calculated by use of the HOSE model and those calculated by use of the quantum-chemical method of Randić ($r = 0.985$, $n = 65$). Analysis of errors shows that only the geometries of molecules estimated with e.s.d.'s for bond lengths $< 0.004 \text{ \AA}$ are sufficiently precise for successful application of the HOSE model. The HOSE model enabled the percentage contributions of the quinoid structure to be estimated for EDA complexes of N,N,N',N' -tetramethyl-*p*-phenylenediamine and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ); in both cases the percentage quinoid form obtained was in line with chemical expectations. For TCNQ salts a good correlation was found between the Flandrois–Chasseau charge at TCNQ species and percentage contribution of the quinoid form calculated by use of the HOSE model ($r = 0.992$, $n = 11$). The HOSE model may serve as a convenient method of prediction and summarization of some chemical properties of molecules of π -electron compounds, directly from experimental geometry.

Introduction

Geometries of π -electron molecules have often been used to discuss their stability. Elvidge & Jackman

(1961) and Sondheimer (1964) have postulated averaging of CC bond lengths as a characteristic feature associated with the higher stability of cyclic π -electron systems (aromatic stability). Julg & François (1967) then introduced a quantitative index, A , describing aromatic stability:

$$A \cong 1 - \frac{225}{n} \sum_{r=1}^n \left(1 - \frac{d_r}{\bar{d}}\right)^2, \quad (1)$$

where \bar{d} is the mean bond length for the n peripheral CC bonds. This idea was then modified in various ways (Julg, 1971; Kruszewski & Krygowski, 1972).

Very recently Krygowski & Więckowski (1981) presented a new approximate way of calculating the stabilization energy of molecules using their geometry directly. The quantity HOSE (Harmonic Oscillator Stabilization Energy) is defined as the negative value of energy necessary to deform the real molecule into its Kekulé (or, more generally, resonance) structure. In other words, HOSE is the energy by which the real molecule is more stable than its Kekulé (or resonance) structure. The following formula was proposed:

$$\text{HOSE} = -E_{\text{def}} = \frac{1}{2} \left[\sum_{r=1}^{n_1} (R'_r - R_o^s)^2 k'_r + \sum_{r=1}^{n_2} (R''_r - R_o^d)^2 k''_r \right], \quad (2)$$

where R'_r and R''_r are the lengths of π bonds in the real molecule, and n_1 and n_2 are the numbers of single and double bonds in the Kekulé structure, respectively. In the process of deformation the n_1 longest bonds are lengthened and the n_2 shortest bonds are shortened to the bond lengths R_o^s and R_o^d , respectively. The latter are those bond lengths which may be assumed as single and double bonds in localized structures of π -electron molecules. The force constants k'_r and k''_r in (2) are calculated by assuming proportionality of k_r and R_r as:

$$k_r = a + bR_r. \quad (3)$$

Table 1. *The constants used in the HOSE model*

Bond	R_o^s (Å)	R_o^d (Å)	a ($\times 10^4$ Pa)	b ($\times 10^4$ Pa)	Remarks*
CC	1.467 (2)	1.349 (1)	44.39	-26.02	C-C and C=C taken from ED data for 1,3-butadiene (a)
CN	1.474	1.274	43.18	-25.73	C-N taken from MW data for CH_3NH_2 (b); C=N taken from ED data for $\text{CH}_2=\text{CH}-\text{CH}=\text{NH}$ (c)
CO	1.428	1.209	52.35	-32.88	C-O taken from ED data for methanol (d); C=O taken from ED data for acroleine (e)

* ED electron diffraction; MW microwave; (a) Kveseth, Seip & Kohl (1980); (b) Pulay & Török (1975); (c) Penn (1978); (d) Kimma & Kubo (1959); (e) Kuchitsu, Fukuyama & Morimo (1969).

Using k_r and R_r for pure single and double bonds, constants a and b have been calculated and are presented in Table 1 together with appropriate reference bond lengths. The choice of the reference bond lengths is in line with the generally accepted definition of resonance energy (Breslow, 1964; Dewar, 1969; Hess & Schaad, 1971*a,b*), which is the difference in energy between the real molecule and its reference structure with localized single and double π bonds. For the practical purpose of calculating the HOSE values we combine equation (3) with (2) and obtain:

$$\text{HOSE} = 301 \cdot 15 \left[\sum_{r=1}^{n_1} (R_r^s - R_o^s)^2 (a + bR_r^s) + \sum_{r=1}^{n_2} (R_r^d - R_o^d)^2 (a + bR_r^d) \right], \quad (4)$$

where the factor $301 \cdot 15$ allows R to be expressed in Å whereas HOSE values are obtained in kJ mol^{-1} .

Extension of the HOSE model

Most molecules with π systems can be described by a few, and sometimes even by many, Kekulé structures. Thus for each resonance structure the calculated HOSE value may be, in principle, quite different. As a consequence the total number of HOSE values which may be calculated for a given molecule equals the number of Kekulé structures taken into account. Hence, following chemical intuition and ideas of the VB (valence-bond) theory the following assumptions are made.

(i) All Kekulé structures have to be taken into account in calculating HOSE for a given molecule:

$$\text{HOSE} = \sum_{i=1}^N C_i \text{HOSE}_i, \quad (5)$$

where summation is over all Kekulé structures (or, more generally, resonance structures). Henceforth HOSE_i stands for the HOSE value of the i th resonance structure.

(ii) The contribution of the i th resonance structure, C_i , in a description of the real molecule is inversely proportional to its destabilization energy*:

$$C_i = \frac{(\text{HOSE}_i)^{-1}}{\sum_{j=1}^N (\text{HOSE}_j)^{-1}}, \quad (6)$$

where summation is over all resonance structures in question. Substituting (6) into (5), after rearrangement one obtains

$$\text{HOSE}^{-1} = N^{-1} \sum_{j=1}^N (\text{HOSE}_j)^{-1}. \quad (7)$$

The physical meaning of HOSE_i may be described as follows: it is the energy by which the real molecule is more stable than its i th Kekulé structure. The less stable a Kekulé structure is (*i.e.* the higher HOSE_i is), the lower is its contribution to the description of the real molecule.

To recognize better the physical meaning of HOSE, the following study was carried out. The stabilization energy for alternant unsaturated hydrocarbons was calculated in three ways and the results are presented in Table 2: first, the direct application of (2) to the geometry of the molecule, *i.e.* irrespective of its Kekulé structures (column 2 of Table 2); second (column 3) HOSE_i was calculated for the Kekulé structure of the lowest energy; third by applying (7) (column 4). When these three sets of data are plotted against resonance-energy values (RE) calculated with the Hess & Schaad (1971*a,b*) method the following correlation coefficients are obtained: $r_1 = 0.895$, $r_2 = 0.955$, $r_3 = 0.991$, respectively. Evidently, application of (7), *i.e.* taking into account all Kekulé structures for a given molecule, yields the best correlation between HOSE and RE.

* The HOSE value describes the stabilization energy of the real molecule with regard to the i th Kekulé structure or describes the destabilization energy of the i th Kekulé structure with regard to the real molecule.

Table 2. HOSE values (kJ mol⁻¹) calculated in three different ways (cf. text)

Compound	HOSE value			RE (Hess & Schaad, 1971a, b)	Reference and method of measurement*	Parameters indicating precision	
	Old method [eq. (2)]	Kekulé structure of lowest energy	Proposed method [eq. (7)]			R	E.s.d.
(1) Ethylene	-0.42	-0.42	-0.42	0	<i>E</i> (a)		
(2) 1,3-Butadiene	0	0	0	0	<i>E</i> (b)		0-002
(3) Benzene	51.41	51.41	51.41	0.39	<i>E</i> (c)		
(4) Benzene (138 K)	51.77	51.77	51.77	0.39	<i>N</i> (d)	0-076	libr.
(5) Benzene (218 K)	51.77	51.77	51.77	0.39	<i>N</i> (d)	0-059	libr.
(6) Benzene (270 K)	55.20	55.20	55.20	0.39	<i>X</i> (e)		
(7) Naphthalene (123 K)	45.74	50.98	75.59	0.55	<i>X</i> (f)	0-047	0-002
(8) Naphthalene	49.03	50.20	73.83	0.55	<i>E</i> (g)		
(9) Perdeuteroanthracene	52.34	71.05	94.96	0.66	<i>N</i> (h)	0-034	0-003
(10) Biphenyl	99.41	109.23	112.16	0.72	<i>X</i> (i)	0-063	0-004
(11) Phenanthrene	71.79	101.79	114.29	0.77	<i>N</i> (k)	0-065	libr.
(12) Phenanthrene	56.16	91.28	120.45	0.77	<i>X</i> (k)	0-060	libr.
(13) Pyrene	75.71	108.53	126.97	0.81	<i>N</i> (l)	0-034	libr.
(14) Pyrene	63.96	109.98	136.24	0.81	<i>X</i> (m)	0-044	libr.
(15) Pyrene (113 K)	73.33	114.68	133.59	0.81	<i>X</i> (n)	0-063	libr.
(16) Chrysene	83.51	99.89	162.03	0.96	<i>X</i> (o)	0-076	libr.
(17) Triphenylene	108.32	144.04	169.30	1.01	<i>N</i> (p)	0-048	0-010
(18) Naphthalene	44.18	48.33	75.41	0.55	<i>E</i> (r)		
(19) Anthracene	85.41	96.43	109.70	0.66	<i>E</i> (r)		
(20) Perylene	104.71	150.09	174.71	0.97	<i>X</i> (s)	0-081	0-010
(21) Coronene	42.10	42.10	186.26	1.27	<i>E</i> (r)		
(22) Ovalene	222.73	222.73	278.92	1.57	<i>E</i> (r)		

* Measurement by: *E*, electron diffraction; *X*, X-ray diffraction; *N*, neutron diffraction. References: (a) Kuchitsu (1968); (b) Kveseth, Seip & Kohl (1980); (c) Tamagawa, Iijima & Kimma (1976); (d) Bacon, Curry & Wilson (1964); (e) Cox, Cruickshank & Smith (1958); (f) Ponomarev, Filipenko & Atovmian (1976); (g) Sehers & Boggs (1981); (h) Lehmann & Pawley (1972); (i) Charbonneau & Delugeard (1977); (k) Kay, Okaya & Cox (1971); (l) Hazell, Larsen & Lehmann (1972); (m) Allmann (1970); (n) Kai, Hama, Yasuoka & Kasai (1978); (o) Burns & Iball (1960); (p) Ferraris, Jones & Yerkess (1973); (r) Almninggen, Bastiansen & Dyvik (1961); (s) Camerman & Trotter (1974); (t) Hazell & Pawley (1973).

For the calculations presented in this paper we have chosen chiefly the most accurate structural data: *i.e.* those with e.s.d.'s for bond lengths ≤ 0.005 Å and for neutron or X-ray diffraction studies additionally those with $R \leq 0.08$.

Equation (6) allows us to calculate contributions of individual structures to the description of the real molecule. These data, C_1 , are compared in Table 3* with the Randić (1977) contributions of the Kekulé structure, calculated by applying quantum-chemical methods. When these two sets of data are plotted against each other, the regression obtained has the form:

$$\% \text{ Kekulé structure (HOSE)} = 0.998 \\ \times [\% \text{ Kekulé structure (Randić)}] + 0.135 \quad (8)$$

with a correlation coefficient $r = 0.985$ for 63 data points. The slope close to 1.00 and intercept close to 0.0 show that these two methods of estimating C_1 values are equivalent in describing the distribution of

the Kekulé-structure contributions. This finding again is especially significant, since the Randić theory originates from quantum chemistry whereas the HOSE model is purely empirical and is based on experimental geometries.

Dependence of HOSE, HOSE_{*i*} and C_{*i*} on experimental errors in bond lengths

From Table 3 it is also clear that percentage contributions of the Kekulé structures, $100C_1$, are less sensitive to the variation in geometry, *i.e.* to experimental errors in bond lengths, than are HOSE_{*i*} values themselves. Nevertheless, it is important to point out that the weighted sum, HOSE, is again less sensitive than HOSE_{*i*}. The problem is illustrated for benzene. Its geometry has been determined by many techniques and at various temperatures. Hence, it is a convenient system for testing the dependence of HOSE on the quality and origin of geometry parameters. Table 4 presents the relevant data. For the X-ray-determined geometry at 270.15 K correction for libration is as large as 0.015 Å (Cox, Cruickshank & Smith, 1958) and hence the difference between HOSE calculated from geometries corrected and uncorrected for libra-

* Table 3 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38538 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tion reaches almost 25%. This difference drops significantly when the geometry is determined by neutron diffraction techniques and at lower temperature: the lower the temperature the smaller the influence on bond lengths of molecular motion. Note the good agreement of HOSE values from geometries corrected for libration with those obtained from electron diffraction or microwave geometries. The range of HOSE values is 3.79 kJ mol⁻¹ which is only 7.3%. When the old X-ray diffraction data are excluded, the range of discrepancy of HOSE values for various experimental geometries of benzene drops to 1.8%. In conclusion one may state that the more reliable HOSE values are those calculated from electron diffraction data or from geometries determined by use of X-ray or neutron diffraction but applying correction for thermal motion. Slightly greater differences in HOSE values are observed for molecules possessing very short CC bonds, but studied by the use of X-ray and neutron diffraction techniques. Bonds with $R_r < 1.375 \text{ \AA}$ are supposed to be a result of systematic shortening in the interpretation of X-ray measurements (Hazell, Larsen & Lehmann, 1972; Więckowski & Krygowski, 1981) and hence quite a considerable difference of 7.2% is observed for HOSE (neutron) and HOSE (X-ray) of pyrene for both of which geometries corrected for effects of thermal motion have been used.

It is also worth mentioning that estimates of e.s.d.'s for HOSE values calculated from the standard theory of error increase quickly with an increase of the e.s.d. of bond lengths. Table 5 presents relevant data which may be summarized in two conclusions: (i) the e.s.d. for HOSE increases about 2–4 times faster than the e.s.d. for bond lengths and (ii) geometries of molecules used to calculate HOSE should not have e.s.d.'s for bond lengths greater than 0.004 Å if HOSE has to have an e.s.d. lower than 5.03/73.0 \approx 7%. With this statement

Table 4. HOSE values for benzene calculated from geometries obtained by various methods and at different temperatures

Measurement method (temperature)	HOSE (kJ mol ⁻¹)	
	Corrected*	Uncorrected*
(1) Electron diffraction data (a)	51.41	—
(2) X-ray diffraction data (b) (270.15 K)	55.20	68.45
(3) Neutron diffraction data (c) (218.15 K)	51.77	56.68
(4) Neutron diffraction data (c) (135.15 K)	51.77	54.48
(5) Microwave data (d)	52.33	—

References: (a) Tamagawa, Iijima & Kimma (1976); (b) Cox, Cruickshank & Smith (1958); (c) Bacon, Curry & Wilson (1964); (d) Stoicheff (1958).

* Bond lengths used in calculations corrected or uncorrected for libration.

Table 5. Dependence of the calculated e.s.d. values for HOSE on e.s.d. values of bond lengths

[Example of naphthalene (Sehers & Boggs, 1981)]

E.s.d. for bond lengths in Å	causes	e.s.d. for HOSE in kJ mol ⁻¹
0.002		1.20
0.004		5.03
0.006		11.3
0.008		20.1

in mind we have chosen most of the examples presented in this paper.

Applications

The HOSE model presented in this paper may be applied to various problems of structural chemistry. A few are presented here.

Non-alternant hydrocarbons

Diffraction studies of non-alternant hydrocarbons are carried out most often with substituted species, since these are easier to synthesize. Table 6 presents HOSE and RE (Hess & Schaad, 1971b) values for a few of them. The comparison with the data for alternant hydrocarbons presented in Fig. 1 leads to the conclusion that the stability of non-alternant systems is overestimated by the HOSE model by about 20–30 kJ mol⁻¹. For these two classes of systems two separate regression lines may be calculated:

$$\text{HOSE} = 169.9 \text{ RE} - 9.8, \quad (9)$$

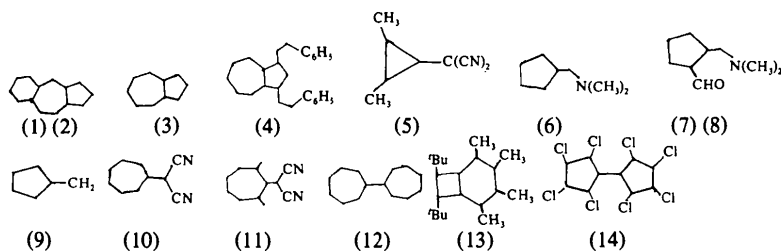
with $r = 0.991$ for 22 alternant hydrocarbons, and

$$\text{HOSE} = 145.7 \text{ RE} + 35.6, \quad (10)$$

with $r = 0.937$ for 12 non-alternant systems. The observed discrepancy is not easy to explain.

Two possible reasons should be mentioned here, however.

(i) Geometries of non-alternant systems are those of their substituted species, with the substituent strongly interacting with the odd ring (*i.e.* a ring containing an odd number of atoms) and stabilizing it according to the $4N + 2$ aromaticity rule, or its extension for polycyclic non-alternant systems (Kruszewski & Krygowski, 1975). This effect is especially well seen for derivatives of fulvene. HOSE for the weakly interacting system 6,6-dimethylfulvene is -0.7 kJ mol^{-1} in comparison with 15.8 kJ mol^{-1} for the strongly interacting system 6-dimethylaminofulvene. A similar effect is expected for (dicyanomethylene)cycloheptatriene. Moreover, if the latter compound is substituted by methyl groups in positions 2,7 which sterically impede resonance interaction between electron-attract-

Table 6. HOSE values (kJ mol^{-1}) for non-alternant systems

Compound	(n)*	HOSE [eq. (16)]	RE (Hess & Schaad, 1971a, b)	Parameters indicating precision		Reference and method of measurement†
				R	E.s.d.	
(1) Benz[<i>f</i>]azulene	(2)	90.68	0.43	0.055	0.008	<i>X</i> (a)
(2) Benz[<i>f</i>]azulene	(2)	98.99	0.43	0.055	0.008	<i>X</i> (a)
(3) Azulene	(2)	85.73	0.23			<i>E</i> (b)
(4) <i>cis,cis</i> -1,3-Distyrylazulene	(2)	92.33	0.23	0.043	0.003	<i>X</i> (c)
(5) 1,2-Dimethyl-3-dicyanomethylenecyclopropene	(1)	26.35	0.02	0.041	0.003	<i>X</i> (d)
(6) 6-Dimethylaminofulvene	(1)	15.79	-0.01	0.045	0.004	<i>X</i> (e)
(7) 6-Dimethylamino-2-formylfulvene	(1)	26.74	-0.01	0.044	0.005	<i>X</i> (e)
(8) 6-Dimethylamino-2-formylfulvene	(1)	29.99	-0.01	0.044	0.005	<i>X</i> (e)
(9) Fulvene	(1)	-0.75	-0.01			<i>E</i> (f)
(10) (Dicyanomethylene)cycloheptatriene	(1)	16.65	-0.02	0.078	libr.	<i>X</i> (g)
(11) 2-Dicyanomethylene-1,3-dimethylcycloheptatriene	(1)	11.84	-0.02	0.086	0.009	<i>X</i> (h)
(12) 1,1'-Bicycloheptatrienyliene	(1)	9.55	-0.20	0.041	libr.	<i>X</i> (i)
(13) 1,2-Di- <i>tert</i> -butyl-3,4,5,6-tetramethylbenzocyclobutadiene	(3)	14.12	-0.22	0.052	0.004	<i>X</i> (k)
(14) Octachlorofulvalene	(1)	-1.42	-0.33	0.036	0.003	<i>X</i> (l)

* Multiplicities of the Kekulé structures, which are equivalent owing to symmetry.

† Measurement by: *X*, X-ray diffraction; *E*, electron diffraction. References: (a) Ammon & Wheeler (1978); (b) Bastiansen & Derissen (1966); (c) Fallon, Ammon, Anderson, Currie & Labar (1974); (d) Ammon, Sherrer & Eicher (1978); (e) Ammon (1974); (f) Baron, Brown, Burden, Donaille & Kent (1972); (g) Shimanouchi, Ashida, Sasada, Murata & Kitahara (1966); (h) Shimanouchi, Sasada, Kabuto & Kitahara (1974); (i) Thomas & Coppens (1972); (k) Winter & Butters (1981); (l) Ammon, Wheeler & Agrant (1973).

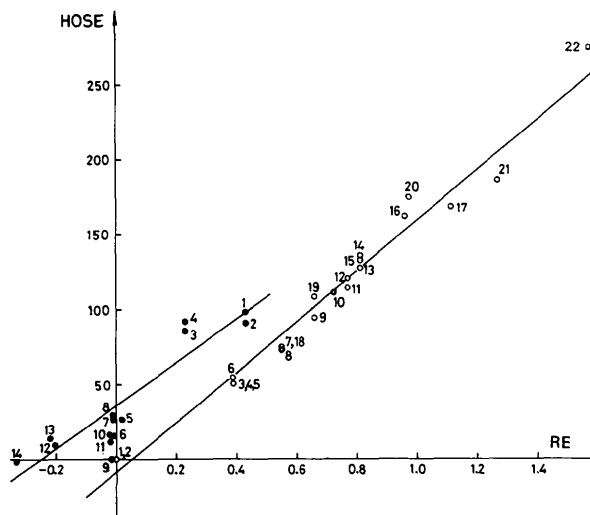


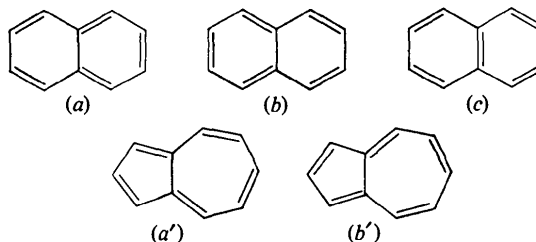
Fig. 1. Plot of HOSE values (kJ mol^{-1}) against the Hess & Schaad (1971a, b) resonance energy (β units) for alternant (open circles) and non-alternant (full circles) hydrocarbons. Assignments as in Tables 2 and 6.

ing CN groups and the electron-releasing odd ring, the HOSE value drops from 17.7 to 11.8 kJ mol^{-1} .

This reason does not apply, however, to the case of unsubstituted non-alternant systems, e.g. azulene,

which according to chemical reasoning and RE expectations is less stable than its valence isomer naphthalene; HOSE values, however, show the reverse result as shown by the data of Tables 6 and 2. The following explanation may partly satisfy the reader.

(ii) A molecule of naphthalene is described by three Kekulé structures (*a*, *b* and *c*), whereas a molecule of azulene is described by only two Kekulé structures (*a'* and *b'*) which are analogous to *a* and *b* for naphthalene.



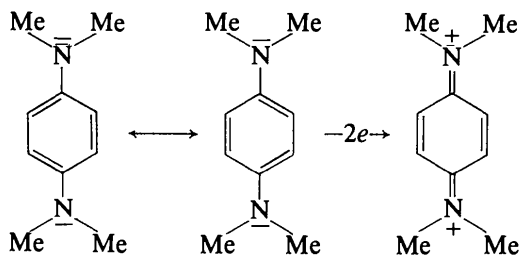
The Kekulé structure (*c*) for naphthalene is most stable ($\text{HOSE}_{i=c} \sim 50 \text{ kJ mol}^{-1}$) and hence this contribution reduces HOSE values for naphthalene. The lack of this Kekulé structure for azulene is a reason for its high HOSE value. Similarly, we observe this effect for all non-alternant systems in Table 6; they are described by

fewer Kekulé structures than their alternant isomers. This shortcoming of the HOSE model may result from taking into account only Kekulé structures. Consideration of non-classical Kekulé and multiply excited structures improves the situation but makes the calculation more complex and the model loses its simplicity.

Electron-donor/electron-acceptor (EDA) complexes

The geometry of donor and acceptor molecules in EDA complexes is expected to vary with the strength of charge-transfer interactions (CT) between the species involved. Two examples are chosen to illustrate this problem.

The donor molecule *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) will interact with acceptor molecules to form EDA complexes and salts, with various degrees of charge transfer. Changes in structure on losing an electron pair are presented schematically below.



Therefore, applying the HOSE model may help in estimating the degree of charge transfer in a given case. In Table 7 it is clearly seen that the percentage contribution of the quinoid form increased from about

20% for TMPD and the weak TMPD–TCNB complex to about 60% for salts in which TMPD exists as a singly charged cation. For the relatively strong complexes $\text{TMPD}^+\cdot\text{TCNQ}^-$ and $\text{TMPD}^+\cdot(\text{TCNQ})_2^-$ the contribution of the quinoid form is about 40%. It appeared strange that for TMPD the contribution of the quinoid form should be as high as 20% but for H_2O (Coulson, 1961) the contribution of the $\text{HO}^- \text{H}^+$ structure in a VB description is 24%.

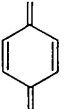
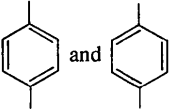
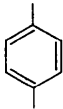
Some data in Table 7 are not too accurate but in spite of this they fit the picture presented above quite well.

Other EDA complexes discussed here very briefly are complexes of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (see Table 8). TCNQ may serve as acceptor and exists in complexes and salts as an anion with various degrees of charge. Flandrois & Chasseau (1977) have published an empirical way of calculating formal negative charges on TCNQ species in EDA complexes based on geometrical data. According to their results negative charges at TCNQ are usually between 0 and -1 or slightly higher (-1.14). Applying the HOSE model for a few EDA complexes and salts with TCNQ as acceptor molecules we have found that the contribution of the quinoid form to the description of the electronic structure is highest for the uncharged TCNQ molecule and drops regularly with increase of negative charge at TCNQ species. For 11 data points we found the linear regression:

$$\% \text{ quinoid form} = -46.2 Q_{\text{Fl}} + 91.2, \quad (11)$$

with correlation coefficient $r = 0.992$. Extrapolation to $Q = 2e$ leads to 1.2% quinoid form and this is in good agreement with expectations based on simple resonance theory.

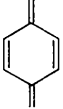
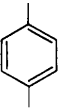
Table 7. HOSE values (kJ mol^{-1}) and Kekulé-structure contributions of TMPD species in various EDA complexes

	Reference	HOSE _t	 (%)	HOSE _t	 and  (%)	HOSE _{tot.}	Parameters indicating precision	
							R	E.s.d.
TMPD*	(a)	140.7	22.04	79.59	77.96	93.1	0.091	0.007–0.012
TMPD–TCNB	(b)	179.7	17.06	73.90	82.94	91.95		
TMPD ⁺ ·ClO ₄ ⁻ (296 K)	(c)	25.66	65.54	97.57	34.46	50.45	0.059	0.006
		61.68	52.06	133.95	47.94	96.33	0.059	libr.
TMPD ⁺ ·ClO ₄ ⁻ (110 K)	(d)	43.67	62.92	148.17	37.08	82.42	0.093	0.003
TMPD ⁺ ·TCNQ ⁻	(e)	70.65	44.66	114.05	55.34	94.67	0.083	0.004–0.014
TMPD ⁺ ·TCNQ ₂ ⁻	(f)	40.17	59.58	118.42	40.41	71.80	0.049	0.004
		74.08	42.16	108.02	57.84	93.71	0.049	libr.
TMPD ⁺ ·I ⁻	(g)	47.22	59.58	139.19	40.22	84.40	0.027	0.006–0.008
TMPD ⁺ ·chloranil	(h)	39.87	60.70	123.74	39.30	72.60	0.076	0.006–0.008

References: (a) Ikemoto (1979); (b) Ohashi, Iwasaki & Saito (1967); (c) de Boer & Vos (1972a); (d) de Boer & Vos (1972b); (e) Hanson (1965); (f) Hanson (1968); (g) de Boer & Vos (1968a); (h) de Boer & Vos (1968b).

* For abbreviations see text; also TCNB: tetracyanobenzene.

Table 8. HOSE model data (kJ mol^{-1}) for a few TCNQ species in EDA complexes and salts, compared with the Flandrois & Chasseau charge Q

Reference	HOSE _i	 (%)	HOSE _i	and  (%)	HOSE _{tot}	Q	Parameters indicating precision		
							R	E.s.d.	
(1) TCNQ ⁰	(a)	6.08	91.28	127.36	8.72	16.65	0	0.039	0.004–0.005
(2) Cs ₂ (TCNQ) ₃ c*	(b)	6.57	91.04	133.26	8.96	17.93	-0.03	0.039	0.004–0.005
(3) nc		32.13	56.45	83.37	43.55	54.41	-0.08		
(4) Rb ₂ (TCNQ) ₃ c	(c)	10.06	84.46	109.38	15.54	25.49	-0.15	0.054	0.002–0.004
(5) nc		34.63	51.06	72.45	48.94	53.05	-0.83		
(6) K(TCNQ)	(d)	42.34	47.12	75.60	52.88	59.86	-0.94	0.044	0.005–0.006
(7)		50.62	39.51	66.45	60.49	60.00	-1.14		
(8) HEM(TCNQ) ₂ †	(e)	15.12	76.99	101.17	23.01	34.92	-0.3	0.071‡	0.003–0.004
(9)		30.36	56.84	79.97	43.16	51.76	-0.63		
(10) DEM(TCNQ) ₂ †	(f)	22.98	66.18	90.42	33.82	45.62	-0.58	0.077‡	0.003–0.004
(11)		22.56	66.28	88.78	33.72	44.85	-0.53		
(12) <i>p</i> -Benzoquinone	(g)	2.59	98.82	430.16	1.20	7.68	0	0.124	libr.
(13) <i>p</i> -Benzoquinone	(h)	2.32	98.91	419.26	1.09	6.88	0	0.074	0.003
(14) γ -Hydroquinone	(i)	236.40	12.86	69.80	87.14	91.23	-2.0	0.085	—

References: (a) Long, Sparks & Trueblood (1965); (b) Fritchie & Arthur (1966); (c) van der Wal & van Bodegom (1979); (d) Konno, Ishii & Saito (1977); (e) van Bodegom & de Boer (1981); (f) Morssink & van Bodegom (1981); (g) Trotter (1960); (h) van Bolhuis & Kiers (1978); (i) Maartmann-Moe (1966).

* c: centrosymmetric; nc: noncentrosymmetric.

† HEM: 4-ethylmorpholinium; DEM: 4,4-diethylmorpholinium.

‡ Higher values of R owing to thermal motion of donor molecules in the complex; TCNQ species are well solved.

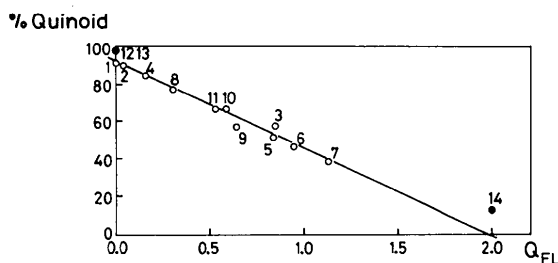
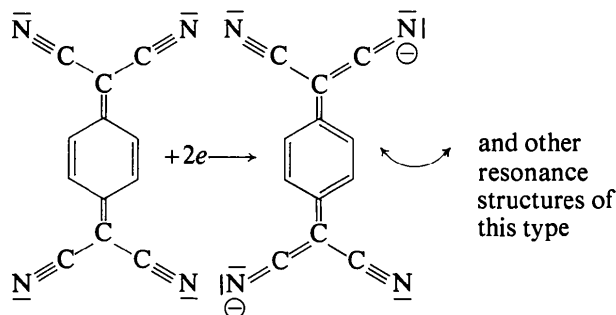


Fig. 2. Plot of percentage of quinoid-form contributions for TCNQ species in EDA complexes and salts against the Flandrois & Chasseau (1977) charge (open circles). For comparison, data for 1,4-benzoquinone and hydroquinone are given (full circles) (see text). Assignments as in Table 8.

A few data in Table 8 are of poor quality, as far as the reliability index R is concerned; its high value is due to thermal motion or disorder of cations; e.s.d.'s of bond lengths for TCNQ species are quite acceptable.



TCNQ species with formal charge -2 are unknown. However, 1,4-benzoquinone belongs to the same group of quinoid compounds and its reduced form hydroquinone may be approximately related to TCNQ²⁻. Included in Fig. 2 are data points for 1,4-benzoquinone and hydroquinone. Both structures have been determined by photographic methods and the precision of their geometries is not too high. Nevertheless, points for these two systems (filled circles) support our former reasoning.

This work was supported by the Polish Academy of Science, project MR. I-9.

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Lattice-Energy Calculations on Phenothiazine and Phenoselenazine Modifications

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(Received 18 April 1983; accepted 13 July 1983)

Abstract

Lattice-energy calculations in the atom–atom potential approach have been performed for observed and isostructurally derived hypothetical forms of pheno-

thiazine and phenoselenazine compounds. Energy minimizations with respect to cell constants and molecular rigid-body coordinates lead to absolute minima of energy surfaces in all cases. The experimental values of cell constants for the three

0108-7681/83/060739-04\$01.50

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