Thermochimica Acta, 51 (1981) 387–389
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

ENERGY PARAMETERS FOR THE π–v TYPE OF CHARGE TRANSFER COMPLEXES

KANCHAN SINGLA *, G.S. GREWAL, ANITA SINGLA and H.S. RANDHAWA

Department of Chemistry, Punjab Agricultural University, Ludhiana 141 004 (India)

(Received 22 May 1981)

In earlier investigations [1–3] we reported the energy parameters for the n–π or π–v ** type of charge transfer (CT) complexes. In the present work we have computed the energy parameters for the CT complexes formed between tetracyanobenzene as v acceptor and various aromatic donors using the method of Sonnessa and Daisey [4] in order to predict the enthalpy of formation (ΔH) of these complexes. The ΔH values were predicted from the empirical formula [3].

$$\frac{b^2}{7.30\,a^2} = -\frac{\Delta H}{h\nu_{CT}}$$

where h is Planck's constant, ν_{CT} is the frequency of the CT band, and a and b are the weighting factors for no bond and dative structures of CT complexes. The agreement between the observed and calculated values of ΔH is good and the average uncertainty is of the order of ± 0.018 eV. The calculated values of energy parameters along with the predicted values of ΔH from the empirical formula are reported in Table 1. The calculated values of ΔH could not be compared with the experimental ones since the latter are not reported in the literature.

It is quite evident from Table 1 that there is small variation found for any one set of energy terms. This effect is apparently due to the relatively small variations in the values of $h\nu_{CT}$ and ΔH among these complexes. With respect to these variations, complexes are classified into three groups: A, strong complexes; B, medium complexes; and C, the weak complexes formed from the respective donors (Table 1). The parameters F, Δ and ΔH for the CT complexes of naphthalene and its derivatives are compared with the σ-Hamett constant of substituents in Table 2, and have been found to follow the order,

naphthalene > dimethoxynaphthalene > diaminonaphthalene.

Further, a number of interesting trends in the calculated values become apparent when comparing A, B and C groups. The value of Δ is found to be inversely proportional to the strength of the complexes and is in agreement with earlier results

---

* Presently with the Plant Breeding Department of the University.

** π–n in ref. 1 should be read as π–v.

0040-6031/81/0000–0000/$02.75 © 1981 Elsevier Scientific Publishing Company

Table 1

Experimental and theoretical energy parameters (in eV except a, b and F) for the CT complexes of tetracyanobenzene acceptor with various π-donors

Donors	$h\nu_{CT}$[a]	Δ	$-X_0$	X_1	G_0	$-\Delta H$[b] (Cal)	a	b	F
Group A									
Analine	2.603	0.729	0.863	1.011	0.649	0.214	0.755	0.585	38.64
	3.619[c]	2.431	0.472	0.716	0.389	0.083	0.895	0.366	16.68
1,4-Diphenylbutadiene	2.665	0.882	0.810	0.973	0.619	0.191	0.774	0.560	35.69
Chrysene	2.689	0.937	0.792	0.960	0.608	0.184	0.781	0.552	34.78
β-Naphthol	2.727	1.020	0.766	0.941	0.592	0.174	0.790	0.539	33.31
Group B									
1,5-Diaminonaphthalene	2.826	1.218	0.709	0.899	0.556	0.153	0.811	0.509	30.04
	3.569[c]	2.364	0.481	0.724	0.396	0.085	0.891	0.372	17.15
Phenantharene	2.900	1.354	0.673	0.873	0.533	0.140	0.824	0.489	27.94
2,7-Dimethoxynaphthalene	2.900	1.354	0.673	0.873	0.533	0.140	0.824	0.489	27.94
Group C									
Durene	3.024	1.566	0.623	0.835	0.499	0.124	0.842	0.461	25.13
Naphthalene	3.037	1.590	0.618	0.829	0.495	0.123	0.844	0.458	24.85
Dimethylanaline	3.037	1.590	0.618	0.829	0.495	0.123	0.844	0.458	24.85
	3.594[c]	2.398	0.476	0.720	0.392	0.084	0.893	0.369	16.92
Pyrene	3.148	1.763	0.582	0.803	0.470	0.112	0.857	0.437	22.85
Anthracene	3.161	1.783	0.578	0.800	0.467	0.111	0.858	0.434	22.56
Diphenyl	3.198	1.839	0.567	0.792	0.459	0.108	0.862	0.428	22.01

[a] Ref. 7; $\beta_0 = -1.20$, $S_{01} = 0.1$

[b] Predicted from the empirical formula

$$\frac{b^2}{7.30\,a^2} = -\frac{\Delta H}{h\nu_{CT}}$$

[c] Corresponds to second CT band.

Table 2

A comparison of the energy parameters of naphthalene and its derivatives with σ-Hamett constant

System	σ	Δ	$-\Delta H$	F
Naphthalene	0	1.590	0.123	24.85
2,7-Dimethoxynaphthalene ($-OCH_3$)	−0.27	1.354	0.140	27.94
1,5-Diamino-naphthalene ($-NH_2$)	−0.66	1.218	0.153	30.04

[1–4]. The positive G_0 values for the systems considered here support the earlier prediction that in stronger complexes with a shorter D–A distance the repulsive forces will predominate over the attractive forces. The increase in the negative value of resonance energy (X_0) in the ground state also follows the trend of ΔH. This is due to an increase of the contribution of resonance interaction and hence CT to the stabilization of the ground state in these complexes which result, in agreement with the theory. The increase in the value of CT, i.e. F, with increasing strength of the complex is also in agreement with the theory.

According to Hanna and Lippert [5] the electrostatic terms make a significant contribution to the energy in the case of weak complexes, which in most cases outweigh the CT resonance contribution since in the stronger complexes the electrostatic terms are operative. The values of X_0 as well as the trend of these values for these CT complexes (Table 1) led us to conclude that CT interactions make a significant contribution to the stability of the ground state like those of n–σ and n–π type complexes [1–4,6]. Conclusions concerning the properties of the excited state dative structure of these complexes could not be drawn since it is difficult to compute the interaction energy G_1 due to unavailability of the vertical ionization potentials of the donors.

REFERENCES

1 H.S. Randhawa, G.S. Grewal, Harpreet Tung and Kanchan Singla, Thermochim. Acta, 44 (1981) 223.
2 H.S. Randhawa, Kanchan Singla, G.S. Grewal and Harpreet Tung, Thermochim. Acta, 45 (1981) 209.
3 H.S. Randhawa, Harpreet Tung and G.S. Grewal, Indian Chem. Manuf., 18 (1980) 8.
4 A.J. Sonnessa and J.M. Daisey, Spectrochim. Acta Part A, 32 (1967) 465.
5 M.W. Hanna and J.M. Lippert, in R. Foster (Ed.), Molecular Complexes, Crane Russak, New York, 1973.
6 H.S. Randhawa and R. Malhotra, Z. Phys. Chem. (Leipzig), 261 (1980) 1, 181.
7 A.S. Bailey, R.J.P. Williams and J.D. Wright. J. Chem. Soc. London, (1965) 2579.