HETEROCYCLES, Vol 19, No 7, 1982

CORRELATION OF SINGLET-TRIPLET TRANSITIONS OF π-ELECTRON HETEROCYCLES WITH THE HMO $N \rightarrow V_1$ ENERGIES

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Abstract — The wavenumbers of the 0—0 bands in the phosphorescence spectra of pyridine-like heterocycles and/or the corresponding bands in their S→T absorption spectra are linearly correlated with the HMO $N \rightarrow V_1$ transition energies, i. e., the transition energies from the highest occupied π-molecular orbital to the lowest unoccupied π-molecular orbital. A similar relationship has been established in the case of thiophene-like heterocycles.

Various semiempirical molecular orbital methods can be used to interpret the electronic absorption and emission (fluorescence, phosphorescence) spectra of organic compounds on quantitative basis. In the case of π-electron systems, the PPP (Pariser—Parr—Pople, LCI-SCF-MO) method has been very successful.[1-5]

However, in spite of the success obtained with the semiempirical methods, the HMO method still represents the simplest approach leading to meaningful empirical correlations of the calculated $E(N \rightarrow V_1)$ values (corresponding to the transition from the highest occupied π-molecular orbital, HOMO, to the lowest unoccupied π-molecular orbital, LUMO) with the energies (usually expressed as wavenumbers) of the longest-wavelength S→S bands in the absorption spectra of conjugated π-electron systems.[6-13] Regression lines obtained for a series of structurally related compounds can be used to predict the wavenumbers or energies of the longest-wavelength bands for compounds for which the experimental absorption curves are not available.

In the HMO method, the energy of $N \rightarrow V_1$ transition represents an average between the $S_0 \rightarrow S_1$ and the $S_0 \rightarrow T_1$ transitions and thus one would also expect a linear correlation between the HMO $N \rightarrow V_1$ transition energies and the wavenumbers of the 0—0 phosphorescence bands and/or the corresponding bands in the S→T absorption spectra of aromatics. Indeed, it has been shown that the wavenumbers of the S→T absorption bands (S→T absorption spectra) or S←T emission bands (phosphorescence spectra) for various π-electron systems are successfully correlated with the HMO $N \rightarrow V_1$ transition energies.[14,15]

It is the purpose of the present communication to show that excellent correlations between the wavenumbers of the S→T bands and the HMO energies are obtained for heterocyclic analogs of benzenoid hydrocarbons treated as individual, structurally homogeneous groups. The group selected for such a correlation are the pyridine-like heterocycles for which a sufficient number of experimental emission and absorption data are available. The experimental wavenumbers of $S_0 \rightarrow T_1$ absorption and emission maxima, the lifetimes of phosphorescence, and the energies of $N \rightarrow V_1$ transitions are summarized in Table 1. In those cases where both the absorption and emission data were available, an average value was used in the correlation. All experimentally observed transitions given in Table 1 are $\pi \rightarrow \pi^*$ transitions. The lowest energy triplet states of pyridine-like heterocycles are known to be π,π^* states and not $\underline{n},\pi^*$ states which usually correspond to higher energy. Thus, the lowest π,π^* triplet state of acridine corresponds to 15.84 kcm^{-1} whereas its $\underline{n},\pi^*$ triplet state is found at 21.40 kcm^{-1}.[16]

Table 1. Wavenumbers of the 0–0 Maxima of Absorption and Emission $S_0 \rightarrow T_1$ Bands, Lifetimes of Phosphorescence (τ_p), and the HMO $N \rightarrow V_1$ Transition Energies for Pyridine-Like Heterocycles

No.	Compound[a]	Absorption (kcm^{-1}) (Ref.)	Emission (kcm^{-1}) (Ref.)	Average[b] (kcm^{-1})	τ_p(sec) (Ref.)	$E(N \rightarrow V_1)$[c] (β Units)
1	Pyridine	29.65 (17)	28.6[d] (18)	29.13	3.2[e](19)	1.841
2	Quinoline	21.85 (17,20)	21.84 (21,22)	21.85	1.3 (22)	1.230
3	Isoquinoline	21.21 (17)	21.38 (21)	21.30	0.9 (22)	1.222
4	Benzo[h]quinoline	21.74 (17)	21.84 (23)	21.79	2.0 (24)	1.187
5	Benzo[f]quinoline	21.88 (17)	21.51 (22)	21.70	3.0 (24)	1.184
6	Phenanthridine	~22.20[f] (17)	20.83 (22)	20.83	1.2 (22)	1.201
7	Benzo[g]quinoline	15.07 (17)	–	15.07	–	0.823
8	Benz[g]isoquinoline	14.87 (17)	–	14.87	–	0.823
9	Acridine	15.84 (25)	–	15.84	~10^{-4} (26)	0.840
10	Thebenidine (4-azapyrene)	16.93 (17)	–	16.93	–	0.782
11	Dibenz[a,h]acridine	–	18.78 (27)	18.78	0.88 (27)	0.931
12	Dibenz[a,j]acridine	–	19.34 (27)	19.34	2.1 (27)	0.990

[a] Ring Index nomenclature is used throughout. [b] This value was used for the correlation in Fig. 1. [c] Calculated by the HMO method, cf. refs.[28,29] The following values were adopted for the Coulomb (α) and resonance (β) integrals: $\alpha_N = \alpha + 0.5\beta$; $\beta_{CN} = \beta$. [d] The value for 2,6-lutidine is 28.16 kcm^{-1}.[19] [e] The value is for 2,6-lutidine. [f] This value was not used in correlation.

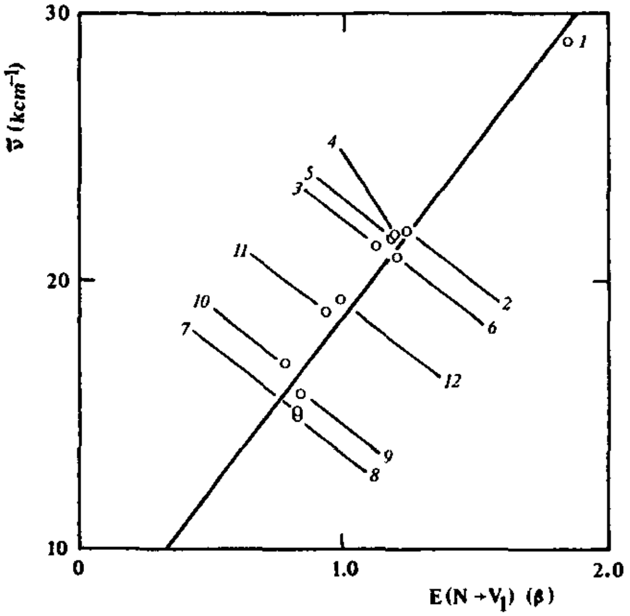

Fig. 1. Plot of wavenumbers of the first maxima of the S→T bands against the *HMO* N→V$_1$ *transition* energies for pyridine-like heterocycles (for numerical values and the designation of compounds, see Table 1).

It can be seen from Table 1 that, in *most cases*, the absorption and emission are quite close and that the average of the two values is then a reasonably reliable quantity for a meaningful correlation which is depicted in Fig. 1. The regression line obtained by the least squares method is

$$(S_0 \rightarrow T_1,\ \mathrm{kcm}^{-1}) = 13.073\ E(N \rightarrow V_1)\ (\beta) + 5.565 \qquad [1]$$

Number of points $\underline{n} = 12$; correlation coefficient $\underline{r} = 0.975$ (the correlation is significant on 1% probability level)

The slope and the intercept of the above regression line are very close to those obtained previously *for a group* of conjugated systems treated as a whole without classification according to the structural types.[15] It is interesting to compare Eq. [1] with the regression line obtained for the longest-wavelength bands in the S→S absorption spectra of pyridine-like heterocycles with the corresponding excitation energies of the N→V$_1$ transitions:[28]

$$(S_0 \rightarrow S_1,\ \mathrm{kcm}^{-1}) = 13.774\ E(N \rightarrow V_1)\ (\beta) + 9.882 \qquad [2]$$

The slopes of the regression lines [1] and [2] are reasonably close.

Another structurally homogeneous group of heterocycles where there is a clear correlation between the S→T absorption and/or emission bands and the E(N→V$_1$) values are the thiophene-like heterocycles. In this case, however, only data for three compounds are available (Table 2).

It should be possible to establish similar correlations for other groups of aromatic heterocycles as soon as enough S→T absorption and/or emission data become available. Correlations of the $S_0 \rightarrow T_1$ transition maxima with the HMO E(N→V$_1$) values can be used to predict energies of $S_0 \rightarrow T_1$ transitions for compounds for which the experimental data are not yet available.

Table 2. Wavenumbers of the 0–0 Maxima of Absorption and Emission $S_0 \rightarrow T_1$ Bands and the HMO $N \rightarrow V_1$ Transition Energies for Thiophene-Like Heterocycles[a]

No.	Compound	Absorption (kcm^{-1}) (Ref.)	Emission (kcm^{-1}) (Ref.)	Average (kcm^{-1})	$E(N \rightarrow V_1)$[b] (β Units)
13	Thiophene	31.25 (30)	–	31.25	1.611
14	Benzo[b]thiophene	23.97 (17)	24.01 (31)	23.99	1.392
15	Dibenzothiophene	24.07 (32)	24.10, 23.20 (33,34)	23.79	1.376

[a] For the regression line for the $S_0 \rightarrow S_1$ bands, see ref.[9] [b] Calculated by the HMO method on a CDC 3100 computer. The model of sulfur which does not allow for the participation of the d-orbitals of sulfur was used.[13] The following values were adopted for the Coulomb (α) and resonance (β) integrals: $\alpha_S = \alpha + \beta$; $\beta_{CS} = 0.7\,\beta$.

ACKNOWLEDGEMENT

Financial support of this work by the Robert A. Welch Foundation, Houston, Texas (Grant No. AH-461) is greatly appreciated.

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Received, 23rd March, 1982