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# A THEORETICAL ANALYSIS OF THE CONFORMATIONS OF MONOSUBSTITUTED NAPHTHALENES

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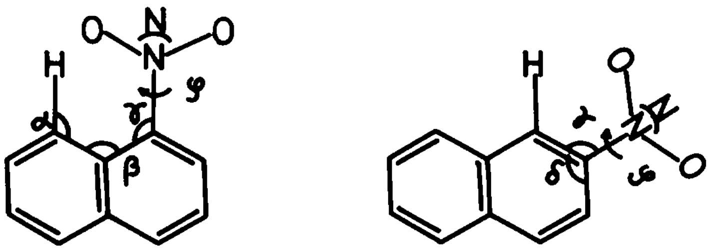
**Abstract**—Valence angles and the angle of twist of the substituent in monosubstituted naphthalenes have been evaluated for the α- and β-isomers of nitronaphthalene, naphthylamine and naphthol by a graphical method. The values of the evaluated angles are as follows: $\angle C_8C_9C_1 (\angle \beta) = 127°$, $\angle C_9C_1N (\angle \gamma) = 123°$, $\angle ONO (\angle N) = 123°$ and the angle of twist of the nitro group ($\angle \phi$) is 50° in α-nitronaphthalene. $\angle \beta = 114°$, $\angle \gamma = 122°$, $\angle HNH (\angle N) = 116°$ and the angle of twist of the amino group ($\angle \phi$) is zero in α-naphthylamine. $\angle C_1C_2N (\angle \gamma) = 120°$, $\angle C_1C_2C_3 (\angle \delta) = 126°$, $\angle ONO (\angle N) = 124°$ and $\angle \phi = 0°$ in β-nitronaphthalene. $\angle \delta = 125°$, $\angle N = 119°$, $\angle \phi = 0°$ in β-naphthylamine. $\angle \delta = 122°$ in β-naphthol. The present calculated values of the angles in α-nitronaphthalene agree closely with Akopyan's calculated values in α-nitronaphthalene and with the observed ones in 1,8-dinitronaphthalene. The influence of twist of the substituent on the electronic spectra has been studied for the monosubstituted naphthalenes.

KITAYGORODSKY and Dashevsky studied theoretically the conformations of cycloalkanes, acenaphthene, polychloronitrobenzenes and monochloronitronaphthalenes.[1-4] Trotter analysed experimentally the conformations of 1,5-dinitronaphthalene α- and β-naphthoic acid.[5,6] Furthermore, he analysed theoretically the steric inhibition of the resonance in nitroanthracene derivatives and nitrobenzene.[7] According to his results, the nitro groups are rotated by 49° about the C—N bonds out of the naphthalene plane in a crystal of 1,5-dinitronaphthalene.[5] The plane of the carboxylic group is rotated through 11° about the C—C bond in α-naphthoic acid, but the plane is not rotated in β-naphthoic acid.[6]

The difference of the molecular structures between α- and β-monosubstituted naphthalenes gives rise to differences in the reactivity, dipole moment and electronic spectrum between these two. It may be of interest to study the steric effect due to the peri-H atom in the α- and β-isomers of nitronaphthalene, naphthylamine and naphthol. The molecular structures of the isomers were determined experimentally only on β-naphthol.[8] In this paper, the angle of twist of the substituent and the valence angles as shown in Fig 1 will be evaluated for the isomers. Moreover, we have studied the influence of twist of the substituent on the electronic spectra of the isomers.

Valence angles, dipole moments and bending force constants have recently been evaluated for some simple molecules by the CNDO method.[9,10] Molecular excited-state geometries and transition energies have also been evaluated for simple molecules by the CNDO method.[11,12] Furthermore, the potential barriers to the internal rotation in the simple molecules ($CH_3CH_3$, $CH_3NH_2$ and $CH_2OH$ etc) were calculated by the LCAO SCF MO method.[13] However, the evaluation of the above molecular constants is not simple for complex molecules by the LCAO MO method. We employed a simplified Dashevsky's method which is simple to estimate the conformations of monosubstituted naphthalenes.



α-Nitronaphthalene β-Nitronaphthalene

FIG 1. The estimated angles of α- and β-nitronaphthalenes. The estimated angles of the other α- and β-substituted naphthalenes are the same as those of α- and β-nitronaphthalenes.

### *Method of calculation and parameters*

The stable conformations of the monosubstituted naphthalenes may be determined graphically by the simplified Dashevsky's method. Dashevsky *et al.* have theoretically determined the conformations of monochloronitronaphthalenes and monochloronaphthoic acids[4] by the use of an electronic computer. Dashevsky's method minimises the sum of the following four energies; (1) the sum of the interaction energies between nonbonded atoms in a molecule, (2) the energy for the deformation of the valence angles, (3) the energy for the displacement of the substituent from a molecular plane and (4) the energy for the rotation of the substituent about a bond.

In the present study, the energy (3) of the four energies was not taken into account, because the calculation is not simple. For the energy (4), we took into consideration not the energy for rotation but the charge-transfer (CT) energy. In Ref 4 the resonance between the substituent and the naphthalene molecule was not taken into account.

In the simplified Dashevsky's method the sum of the following three kinds of energies was minimized.

(1) The energy for the deformation of the valence angles. $E_1$.

The energies for the deformation of the valence angles, such as the C—C—C and H—C—C valence angles, can be evaluated by the following equation.

$$E_1 = 1/2 \sum_{i} C_i(\Delta\varepsilon_i)^2 \tag{1}$$

$\Delta\varepsilon_i$ represents the change in the valence angle from its normal angle for the atom i. $C_i$ is the bending force constant determined by Kitaygorodsky,[2,3] and its value is shown in Ref 4.

(2) The sum of the dispersion and repulsion interaction energies between nonbonded atoms in a molecule is $E_2$. The sum of the interaction energies $E_2$ is given by

$$E_2 = \sum_{l,m} f_k(r_{lm}) \tag{2}$$

$f_k(r_m)$ is the interaction energy between nonbonded atoms l and m, $r$ is the interatomic distance, and k represents the kind of the pair of different atoms between l and m. The following form is used for the practical calculation of $f_k(r_{lm})$

$$f_k(r_{lm}) = -Mr^{-6} + N\exp(-qr) \tag{3}$$

where $M$, $N$ and $q$ are the parameters which have the values shown in Ref 4.

(3) The CT energy for the different angles of twist of the substituent is $E_3$.

We studied theoretically the influence of twist of the substituent on the electronic spectra for the monosubstituted naphthalenes. The intensities and positions of bands were calculated for the different angles of twist of the substituent. The calculation was to evaluate the interaction energy among several electron configurations in a molecule. The method of calculation is the one developed by Pople,[14] and by Longuet-Higgins and Murrell.[15] The configurations include the ground, locally excited and CT configurations. The energy level of the ground configuration is dropped down by the stabilization of the energy. The CT energy $E_3$ is approximately equal to the stabilization energy of the ground configuration.

In order to simplify the calculation, we took the configurations only, $B_{2u}^-$, $B_{2u}^+$, $B_{3u}^-$ and $B_{3u}^+$, corresponding to the allowed transitions for the locally excited configurations of the naphthalene molecule. We took two kinds of the CT configurations. They are caused by an electron transfer from the occupied orbitals ($\phi_4$ and $\phi_5$) of naphthalene to the vacant orbital of the nitro group ($\phi(NO_2)$) in α- and β-nitronaphthalenes (these CT configurations are abbreviated to $CT_4$, $CT_5$). The two kinds of the CT configurations were also taken for the α- and β-isomers of naphthylamine and naphthol. They are caused by an electron transition from the 2pπ orbital of the substituent to the lowest vacant orbitals ($\phi_6$ and $\phi_7$) of the naphthalene molecule (these CT configurations are abbreviated to $CT_6$, $CT_7$).

The intensity and position of the electronic absorption bands were estimated for 6 monosubstituted naphthalenes for different angles of the substituent. One of their results is shown in Fig 2. In Fig 2 A, B, C and D represent the positions and the oscillator strengths of each absorption corresponding to the transition. A′, B′... represent the calculated ones. We call them the A,B ... bands and A′, B′... bands,

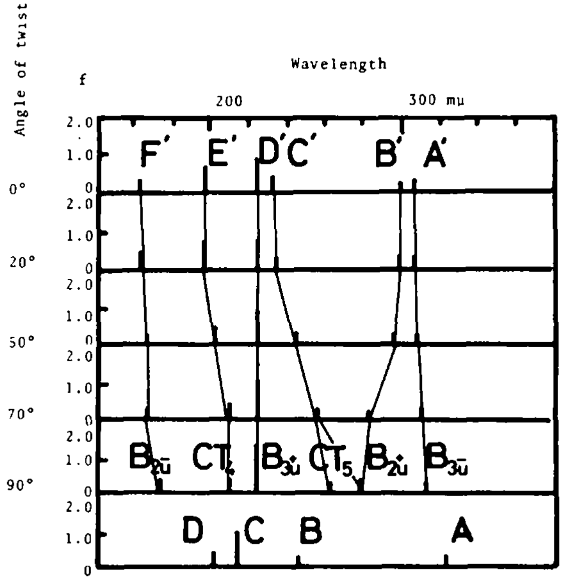


FIG 2. Variation of the calculated intensities and positions of the bands for the different angles of twist of the nitro group and comparison with the experimental intensities and positions of the bands for α-nitronaphthalene.[19]

respectively. The values of the resonance integrals used in the calculation were taken from the theoretical studies of the electronic energies of nitrobenzene,[16] aniline[17] and phenol.[17]

The most stable conformations of the monosubstituted naphthalenes must satisfy the following condition.

$$\begin{aligned}\partial E/\partial(\Delta\varepsilon_j) = {} & \sum_{i} C_i\Delta\varepsilon_i\, \partial(\Delta\varepsilon_i)/\partial(\Delta\varepsilon_j) + \\ & \sum_{lm} \partial f_k(r_{lm})/\partial r_{lm}\, \partial r_{lm}/\partial(\Delta\varepsilon_j) + \\ & \partial E_3/\partial(\Delta\varepsilon_j) = 0 \end{aligned} \tag{4}$$

If $f_k(r_{lm})$ and $E_3$ are taken as the function of $\Delta\varepsilon_j$, Eq. 4 for $\Delta\varepsilon_j$, $\Delta\alpha$, $\Delta\beta$, . . ., is represented by 6 simultaneous equations:

$$\begin{aligned} \partial E/\partial(\Delta\alpha) &= C_\alpha\Delta\alpha + \sum_{lm} \partial f_k(r_{lm})/\partial r_{lm}\, \partial r_{lm}/\partial(\Delta\alpha) = 0 \\ \partial E/\partial(\Delta\beta) &= C_\beta\Delta\beta + \sum_{lm} \partial f_k(r_{lm})/\partial r_{lm}\, \partial r_{lm}/\partial(\Delta\beta) = 0 \\ &\ \vdots \\ \partial E/\partial(\Delta\phi) &= \sum_{lm} \partial f_k(r_{lm})/\partial r_{lm}\, \partial r_{lm}/\partial(\Delta\phi) + \partial E_3/\partial(\Delta\phi) = 0 \end{aligned} \tag{5}$$

E is the total energy $E = E_1 + E_2 + E_3$, $\alpha$, $\beta$ and $\phi$ are the angles shown in Fig 1, and $\Delta\alpha$, $\Delta\beta$ and $\Delta\phi$ are their variations. We assumed that the variation of $E_3$ depends only on $\Delta\phi$. $\partial E/\partial(\Delta\alpha)$, $\partial E/\partial(\Delta\beta)$ and $\partial E/\partial(\Delta\phi)$ were graphically obtained by plotting E against $\Delta\alpha$, $\Delta\beta$ and $\Delta\phi$, respectively, and $\partial E_3/\partial(\Delta\phi)$ was obtained by plotting $E_3$ against $\Delta\phi$ (variation from the molecular plane).

## RESULTS AND DISCUSSIONS

*Estimation of the valence angles.* Figs 3, 4, 5 and 6 summarize the variation of the energies against the variation of the valence angle from its normal angle. The curves in Figs 3, 4 and 5 have the minimum values at $+3°$ for $\Delta\gamma$, $+7°$ for $\Delta\beta$ and $+3°$ for $\Delta N$ in α-nitronaphthalene, respectively, and the minimum value is not very clear for $\Delta\alpha$. From the results obtained, we may conclude that $\angle\beta = 127°$, $\angle N = 123°$ and the value of $\angle\alpha$ is ambiguous for α-nitronaphthalene. For β-nitronaphthalene, the minimum values for the curves are obtained at $\Delta\gamma = 0°$, $\Delta\delta = +6°$ as is shown in Fig 5. Thus, $\angle\gamma = 120°$, $\angle\delta = 126°$ are obtained for this molecule. The angle of twist of the substituent was evaluated to be $\angle\phi \simeq 50°$ for α-nitronaphthalene, $\angle\phi = 0°$ for β-nitronaphthalene as can be seen in Fig 6. Table 1 summarizes the results obtained for the monosubstituted naphthalenes and a comparison of these results with the other related theoretical and experimental data. The estimation of the angles for α-nitronaphthalene may be reasonable because the present calculated values of the angles agree closely with Akopyan's calculated result of α-nitronaphthalene and with Trotter's observed angles of 1,5-dinitronaphthalenes given in Table 1. The estimated

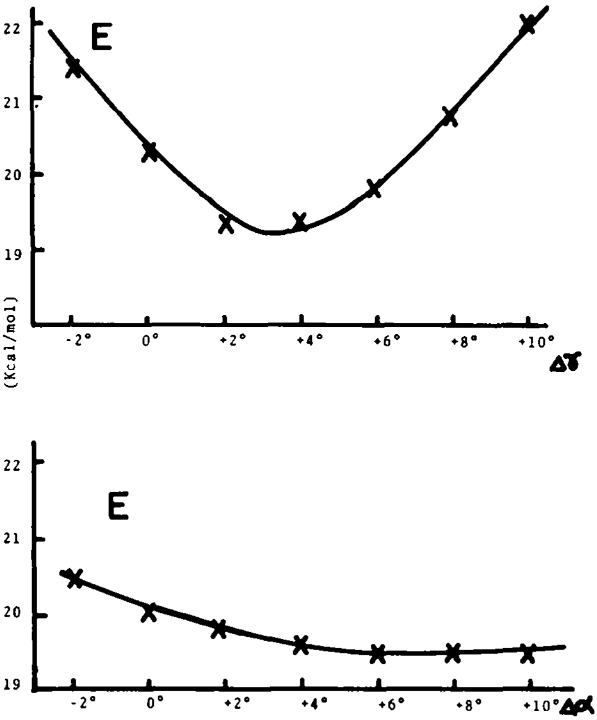


FIG 3. The plots of $E( = E_1 + E_2)$ vs $\Delta\alpha$ and $E( = E_1 + E_2)$ vs $\Delta\gamma$ for α-nitronaphthalene.

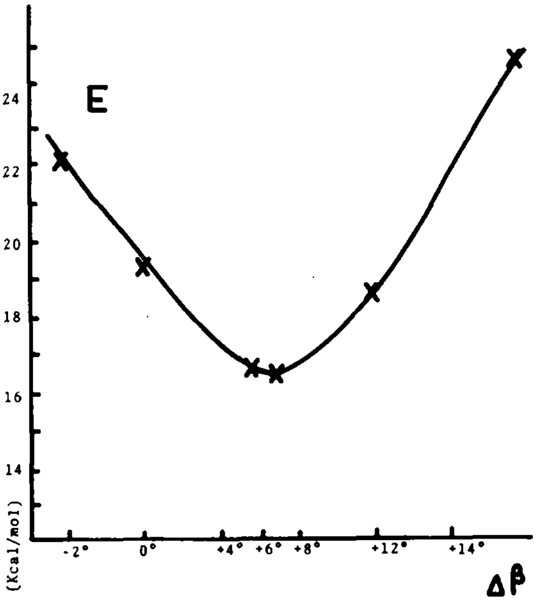


FIG 4. The plots of $E( = E_1 + E_2)$ vs $\Delta\beta$ for α-nitronaphthalene.

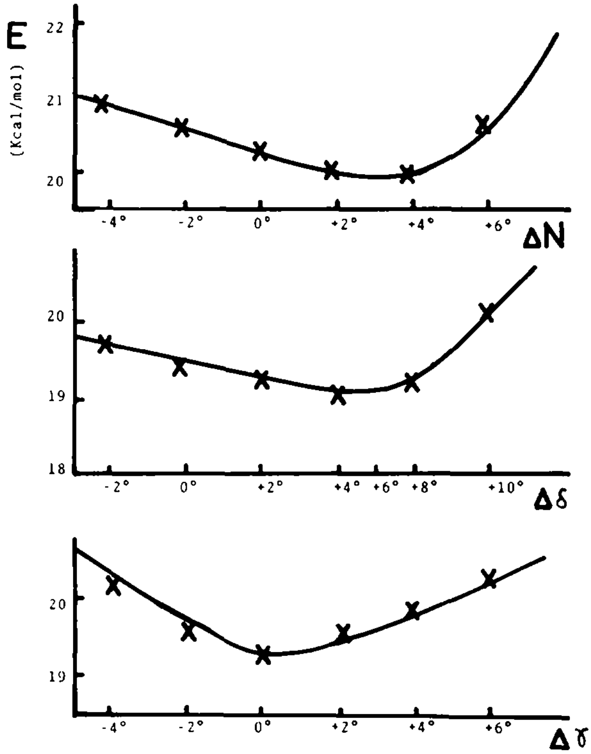


FIG 5. Plots of E *vs* ΔN for α-nitronaphthalene and of E *vs* Δδ and E *vs* Δγ for β-nitronaphthalene.

angle of twist of the substituent for β-nitronaphthalene and β-naphthylamine (both $\angle\phi = 0°$) may be reasonable, because the angle of twist is known to be very small for the β-isomer.[6] Considering the observed angle of twist of the carboxylic group in α-naphthoic acid ($\angle\phi = 11°$),[6] we see that the estimated angle of twist of the amino group is small in α-naphthylamine. The observed valence angle of the amino group ($\angle N = 113°$)[18] is smaller than its normal value (120°). The present calculated valence angle of the amino group ($\angle N = 116°$) is also smaller than its normal value for α-naphthylamine in Table 1. The observed angles of $\angle\delta$ (or $\angle\beta$) and $\angle C$ (C means of the angle OCO) in β-naphthoic acid[6] are a little larger than those in α-naphthoic acid. The present calculated angles of $\angle\delta$ and $\angle N$ in β-naphthylamine are a little larger than those in α-naphthylamine. The same tendency as described above can be seen between α- and β-naphthol for the calculated angles.

### *The influence of twist of the substituent to the electronic spectra*

Fig 2 shows the variation of the calculated oscillator strengths and positions of the absorption bands of α-nitronaphthalene for the angles of twist of the nitro group. The variation of the oscillator strengths and positions of the bands were also evaluated in β-nitronaphthalene and in the α- and β-isomers of naphthylamine and naphthol.

*α-nitronaphthalene.* As the angle of the twist increases, the excitation energy corresponding to the C′ band greatly affected by the increase of the contribution of the $B_{2u}^{+}$

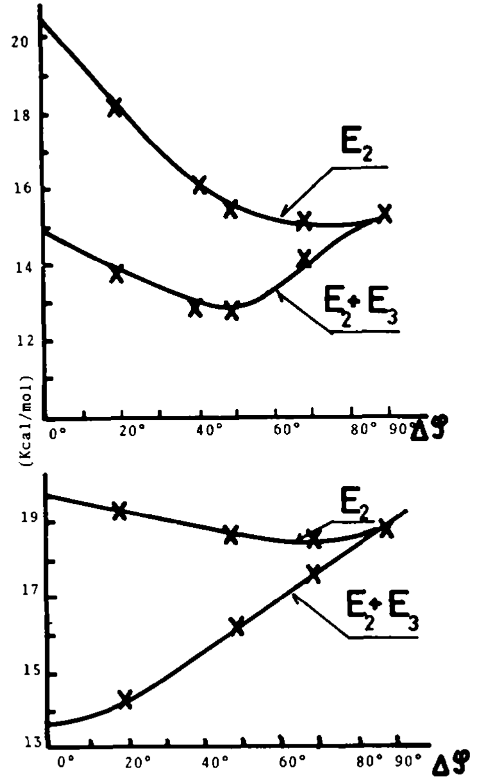


FIG 6. Plots of $E(E_2 + E_3)$ *vs* $\Delta\phi$ for α- and β-nitronaphthalenes. Upper figure... α-nitronaphthalene, lower figure... β-nitronaphthalene.

configuration. The $B_{2u}^+$ configuration contributes greatly to the excitation energy corresponding to the C′ band in the range of $\angle\phi > 50°$. The angle of twist of the nitro group ($\angle\phi = 50°$) was estimated as shown in Table 1, and the assignment of all the bands at $\angle\phi = 50°$ is as follows. Main configurations contributing to the excitation energies for each band are written in parentheses. The A band corresponds to the overlapping of the A′ ($B_{3u}^-$ and $B_{2u}^+$) and the B′ ($B_{2u}^+$ and $CT_5$) bands. The B band corresponds to the C′ band ($B_{2u}^+$ and $CT_5$), the C band to the D′ band ($B_{3u}^+$ and $CT_4$), and the D band to the E′ band ($CT_4$ and $B_{3u}^+$). The estimation of the intensities and positions of all the bands almost agree with those of Kojima.[19]

*α-naphthylamine.* The A band (at 320 mμ) may correspond to the overlapping of the A′ (at 320 mμ, $B_{3u}^-$) and the B′ (at 300 mμ, $B_{2u}^+$) bands. The position of the B′ band shifts from 300 to 280 mμ with the increase of the twist of the amino group. The position of the C′ band ($CT_6$) shifts from 205 to 245 mμ with the increase of the twist. The position of this band is in the longer wavelength side than that of the D′ band (at 215 mμ, $B_{3u}^+$) in the range of $\angle\phi > 40°$. The C′ band may correspond to the B band by considering the intensity and position of the bands.

*α-naphthol.* The D′ band (at 195 mμ, $CT_6$ and $B_{2u}^+$) may correspond to the C band (at 230 mμ) by considering the intensity and position of bands. The position of the D′ band shifts from 195 mμ with the increase of the twist of the OH group.

TABLE 1. THE VALUES OF ESTIMATED ANGLES (IN DEGREE) AND THE COMPARISON WITH THE RELATED DATA

| Author | α | β | γ | δ | N(C)[a] | φ | Molecule |
|---|---|---|---|---|---|---|---|
| Present Study | — | 127 | 123 | / | 123 | 50 | α-Nitronaphthalene |
| (calc.) | — | / | 120 | 126 | 124 | 0 | β-Nitronaphthalene |
| | — | 114 | 122 | / | 116 | 0 | α-Naphthylamine |
| | — | / | / | 125 | 119 | 0 | β-Naphthylamine |
| | — | 114 | 121 | / | / | 80 ~ 100 | α-Naphthol |
| | — | / | / | 122 | / | — | β-Naphthol |
| Watson *et al.*[b] (exp.) | 123 | / | / | 121 | / | — | β-Naphthol |
| Akopyan *et al.*[c] (calc.) | 122·6 | 125 | 121·8 | / | 124 | 45 | α-Nitronaphthalene |
| Trotter[d] (exp.) | — | 126 | 121 | / | 123 | 49 | 1,5-dinitronaphthalene |
| Akopyan *et al.*[c] (exp.) | — | 127·5 | 121 | / | 124 | 45 | 1,8-dinitronaphthalene |
| Trotter[e] (exp.) | — | 115 | 128 | / | 110 | 11 | α-Naphthoic acid |
| Trotter[e] (exp.) | 120 | / | / | 118 | 112 | 0 | β-Naphthoic acid |

[a] C means ∠OCO for naphthoic acid.

[b] Ref. 8.

[c] Z. A. Akopyan, A. I. Kitaygorodsky and Yu. T. Struchkov, *Z. Strukt. Khimi USSR* **6**, 729 (1965).

[d] Ref. 5.

[e] Ref. 6. The dash and slanting stroke mean the results are ambiguous and that there is no angle.

β-*nitronaphthalene.* The assignment of the bands and the estimation of the intensities and position of the bands are almost the same as those of Kojima.[19] The position of almost all the bands is not affected by the twist of the nitro group.

β-*naphthylamine.* The position of the D′ band ($CT_6$ and $B_{3u}^+$) shifts from 190 mμ to 220 mμ with an increase of the twist of the amino group. There are no bands which suffer a contribution from the CT configurations in the all bands.

β-*naphthol.* There is no band which suffers a great contribution from the CT configurations. The intensity and position of all bands are not affected by the twist of the OH group.

*Expansion of the charge-transfer energy by cos φ*

The plots of $E_3$ against $\phi$ are shown in Fig 7. Table 2 shows the equations of $E_3$ expanded in a power series of $\cos\phi$ to the fifth-order terms. The expansion coefficients were determined by solving the simultaneous equations for $E_3$ and $\cos \phi$. The CT energies are nearly equal to 2·5 Kcal/mol for α-nitronaphthalene at $\angle \phi = 50°$, and 6·0 Kcal/mol for β-nitronaphthalene, 5 Kcal/mol for α-naphthylamine, and 4 Kcal/mol for β-naphthylamine at $\angle\phi = 0°$. The expansion terms of the maximum contribution to the CT energies are as follows at each estimated angle of twist. They are the terms of $\cos^2\phi$ for α-nitronaphthalene, $\cos^4\phi$ for β-nitronaphthalene and $\cos^2\phi$ for β-naphthol. The terms of $\cos^2\phi$ and $\cos^3\phi$ contribute to $E_3$ for nitrobenzene at $\angle\phi = 0°$. This conclusion for nitrobenzene is almost equal to Trotter's conclusion which is that the resonance energy between the substituent and the benzene ring is approximately proportional to $\cos^2\phi$.

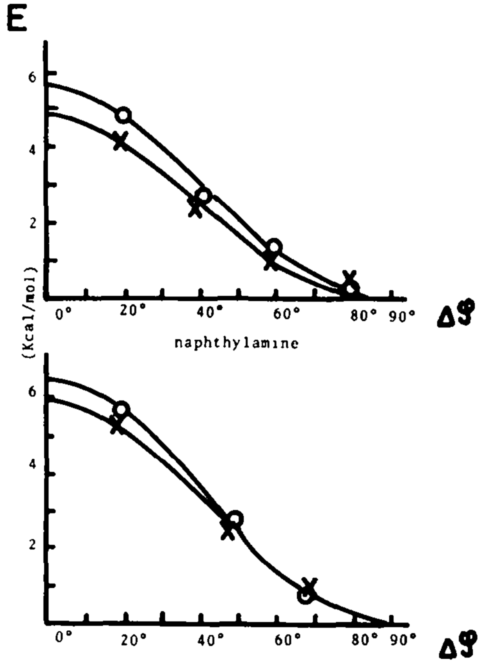


FIG 7. The plots of $E_3$ *vs* $\phi$ for nitronaphthalene and naphthylamine. -○-... α-derivatives, - x -... β-derivatives.

TABLE 2. EXPANSION EQUATION OF $E_3$ BY COS $\phi$

$$E_3 = -0{\cdot}477\cos\phi + 12{\cdot}244\cos^2\phi + 2{\cdot}036\cos^3\phi - 24{\cdot}034\cos^4\phi + 16{\cdot}632\cos^5\phi$$
(for nitronaphthalene)

$$E_3 = 20{\cdot}141\cos\phi - 36{\cdot}154\cos^2\phi - 61{\cdot}848\cos^3\phi + 172{\cdot}854\cos^4\phi - 89{\cdot}598\cos^5\phi$$
(for naphthylamine)

$$E_3 = -14{\cdot}140\cos\phi - 26{\cdot}012\cos^2\phi - 42{\cdot}625\cos^3\phi + 118{\cdot}990\cos^4\phi - 89{\cdot}883\cos^5\phi$$
(for naphthol)

$$E_3^* = -56{\cdot}114\cos\phi + 226{\cdot}155\cos^2\phi - 241{\cdot}672\cos^3\phi + 23{\cdot}153\cos^4\phi + 54{\cdot}478\cos^5\phi$$
(for nitrobenzene)

[*] The data $E_3$ *vs* $\phi$ on nitrobenzene are used from Trotter's result.[7]

### *Discussion of the method of calculation*

*Mathematical determination of* $\Delta\varepsilon_i$. We consider the energies of the dispersion and repulsion interaction between the nonbonded atoms $H_1$ and $H_2$ in Fig 8. The distance

$r(H_1H_2)$ as a function of $\Delta\alpha$ (variation of the valence angle) can be obtained as follows.

$$\begin{aligned} r(H_1H_2) &= \surd[2 \times 1{\cdot}08^2 - 2 \times 1{\cdot}08^2\cos(120^\circ + \Delta\alpha)] \\ &= \surd[2{\cdot}33(1 + \sin(30^\circ + \Delta\alpha))] \end{aligned} \tag{6}$$

The trigonal function in Eq 6 can be simplified by using the first approximation of the well known relation.

$$\begin{aligned} \sin(\Delta\alpha) &= \Delta\alpha - (\Delta\alpha)^3/6 + \dots \\ \cos(\Delta\alpha) &= 1 - (\Delta\alpha)^2/2 + \dots \end{aligned} \tag{7}$$

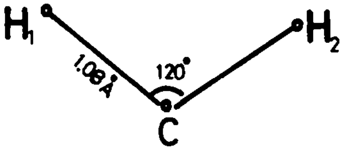


FIG 8. Some single bonds between carbon and hydrogen atoms having the valence angle 120°. The bond length and the valence angle were taken for methyl acrylate[21].

Then Eq 6 is

$$\begin{aligned} r(H_1H_2) &= \surd 2{\cdot}33\,(1 + \sin30^\circ + \Delta\alpha\cos30^\circ)] \\ &= \surd\,[2{\cdot}33\,(1 + \sin30^\circ) + 2{\cdot}33\,\Delta\alpha\cos30^\circ] \\ &= r_0(H_1H_2) + 1/2\ 2{\cdot}018\,\Gamma\alpha \\ &= r_0(H_1H_2) + 1{\cdot}009\,\Delta\alpha \end{aligned} \tag{8}$$

$r_0(H_1H_2)$ is the equilibrium distance of $r(H_1H_2)$. In general, we may write $r_{lm}$ as a function of $\Delta\alpha$ when the valence angle $\alpha$ is varied by $\Delta\alpha$.

$$r_{lm} = r_0 + a_i\,\Delta\alpha \tag{9}$$

$a_i$ is a coefficient. Eq 9 is substituted into $r$ of Eq 3, then the dispersion and repulsion interaction energies between nonbonded atoms can be represented as the function of $\Delta\varepsilon_i$.

$$f_k = -M/(r_0(l, m) + a_i\Delta\varepsilon_i)^6 + N\exp\{-q(r_0(l, m) + a_i\,\Delta\varepsilon_i)\} \tag{10}$$

Then Eq. 5 can be written as follows

$$\begin{aligned} \partial E/\partial(\Delta\alpha) &= C_\alpha\,\Delta\alpha + \sum_{lm} \{6M\,a_1/(r_0(l, m) + a_1\,\Delta\alpha)^7 - \\ &\qquad Na_1q\exp^{[-qr_0(l,\ m)]}\exp^{[-qa_1\Delta\alpha]}\} = 0 \\ \partial E/\partial(\Delta\beta) &= C_\beta\Delta\beta + \sum_{l,\ m} \{6Ma_2/(r_0(l, m) + a_2\Delta\beta)^7 - \\ &\qquad Na_2q\exp^{[-qr_0(l,\ m)]}\exp^{(-qa_2\Delta\ \beta)}\} = 0 \\ &\ \vdots \end{aligned} \tag{11}$$

$\Delta\alpha$, $\Delta\beta$ are determined mathematically by solving the above simultaneous equations. It is difficult to solve the equations mathematically. The present graphical solving is a simple method which can solve the above difficult equations by finding the minimum points of the curves corresponding to the variation $\partial E/\partial(\Delta\alpha)$ and $\partial E/\partial(\Delta\beta)$.

*Evaluation of the charge-transfer energy* $E_3$. The stabilization energy ($\Delta E$) was obtained by a rather complicated method presented in this paper. This energy can be evaluated by a simple method[20] as follows.

$$\Delta E = 1/2\{H_D - V_A + \{(H_D - V_A)^2 + (2C_DC_A\beta_{AD})^2\}^{1/2} \qquad (12)$$

D,A represent the donor and the acceptor molecules, and H,V the highest occupied and the lowest vacant orbitals of the molecules, respectively. C is the coefficient of the molecular orbitals. $\beta$ is the resonance integral between the donor and the acceptor molecules. $E_3$ is estimated as twice the stabilization energy $\Delta E$.

*Accuracy of the calculation.* Dashevsky[4] determined the conformations of monosubstituted nitronaphthalenes and monosubstituted nitrobenzenes by the calculation. It is confirmed in Ref 4 that the agreement of the calculated values of the valence angles with the experimental ones is good in the range of $\angle\phi = 15° \sim 60°$ for monosubstituted nitronaphthalenes. The following discussion was also made in Ref 4. The H-bonding and the packing effect in a crystal must be taken into consideration in the range of $\angle\phi < 15°$, and the approximation of the calculation is not good in $\angle\phi > 60°$. The same discussion as described above may be applied to the results of the present calculation. The minimum point of the curve of E *vs* $\Delta\varepsilon_i$ may be within $\pm 1°$ except that of E *vs* $\Delta\phi$.

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