[5] *A. R. Olson & R. J. Miller*, J. Amer. chem. Soc. *60*, 2690 (1938).
[6] *L. R. Barclay, N. D. Hall & G. A. Cooke*, Can. J. Chemistry *40*, 1981 (1962).
[7] *J. F. Bunnet, M. M. Robison & F. C. Pennington*, J. Amer. chem. Soc. *72*, 2378 (1950).
[8] *E. Taschner & B. Liberek*, Roczniki Chem. *30*, 323 (1956).
[9] *E. Cherbulliez, J. P. Leber & M. Bouvier*, Helv. *36*, 1203 (1953).
[10] *F. Elsinger, J. Schreiber & A. Eschenmoser*, Helv. *43*, 113 (1960).
[11] *C. K. Ingold* "Structure and Mechanism in Organic Chemistry», 2nd Ed., Cornell University Press, Ithaca, N.Y. (1969).
[12] *E. C. F. Ko & A. J. Parker*, J. Amer. chem. Soc. *90*, 6447 (1968).
[13] *D. H. McDaniel & H. L. Brown*, J. org. Chemistry *23*, 420 (1958).
[14] a) *H. H. Jaffé*, Chem. Rev. *53*, 191 (1953); b) *H. van Bekkum, P. E. Verkade & B. M. Wepster*, Rec. Trav. chim. Pays Bas *78*, 815 (1959).
[15] *J. Delhoste*, Bull. Soc. chim. France, 133 (1974).

108. Photoelectron Spectroscopy of *peri*-Amino Naphthalenes

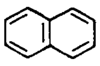
by **John P. Maier**

Physikalisch-Chemisches Institut der Universität Basel

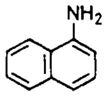
(16 XI. 73)

Summary. The He I photoelectron spectra of *peri*-amino and dimethylamino naphthalenes are presented. The differences in the ionization energies of the π-bands are interpreted by separation of the perturbation of the amino substituent into an inductive destabilization and conjugative stabilization. This affords the assignment of the photoelectron bands of ionization energies below 11 eV and an estimation of the dihedral angle in the *peri*-dimethylamino derivatives. The data on the *peri*-amino naphthalenes indicate some angular distortion in contrast to 2-aminonaphthalene.

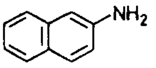
Introduction. – *peri*-Substituted naphthalenes provide an example of molecules where intramolecular crowding can be considerable. The proximity of the *peri*-substituents (*i.e.* 1,8 positions) often results in unique physicochemical properties [1]. For example, 1,8-bis(dimethylamino)naphthalene (**8**) has been found to have an abnormally high basicity, $pK_a = 12.34$ [2], which has been associated with relief, of steric strain and of nitrogen lone-pairs interactions, on protonation.



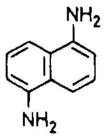
1



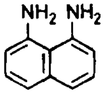
2



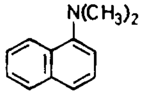
3



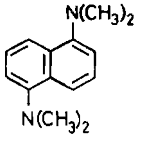
4



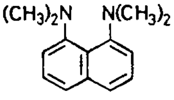
5



6



7



8

Photoelectron (PE.) spectroscopy can be a useful technique for discussion of conformations, as well as of the electronic structure, in the vapour phase when bands in the spectra are sensitive to conformational changes in a comprehensible manner [3]. The study by PE. spectroscopy of the π-ionization energies (IE's) in series of sterically hindered benzenes [4–6] demonstrated that steric and electronic effects may be separated to a degree and a reasonable estimation of the equilibrium conformation attained. Then the study of the electronic structure by PE. spectroscopy of the *peri*-aminonaphthalenes is expedient to elucidate the changes of conformation of the *peri*-substituents due to the interplay of conjugation, intramolecular steric strain, and in the 1,8-diamino cases, the direct interaction of the nitrogen lone-pairs.

Experimental Results. – The He I PE. spectra are reproduced in Fig. 1 and 2, and the IE's are presented in Tab. 1. The band maxima are referred to as the vertical IE's (used in the discussion) and the band onset (adiabatic IE's) are listed in parentheses in Tab. 1, when defined in the spectra. The values quoted are estimated uncertain to ±0.05 eV for the broad bands, unless extensive overlapping occurs in which case to ±0.1 eV. The band numbering in Tab. 1 refers to that in Fig. 1 and 2. The assignments are summarized in the correlation diagram of Fig. 3, and are labelled according to the symmetry species of C_{2v} and C_{2h} for the 1,8 and 1,5 substituted molecules respectively.

Table 1. *Ionisation Energies (eV) of the naphthalenes* **2** *to* **8**

The numbering of the bands ⓘ in Fig. 1 and 3 correspond to the index i of the ionisation energies I_i. The values listed in parentheses are the adiabatic ionisation energies.

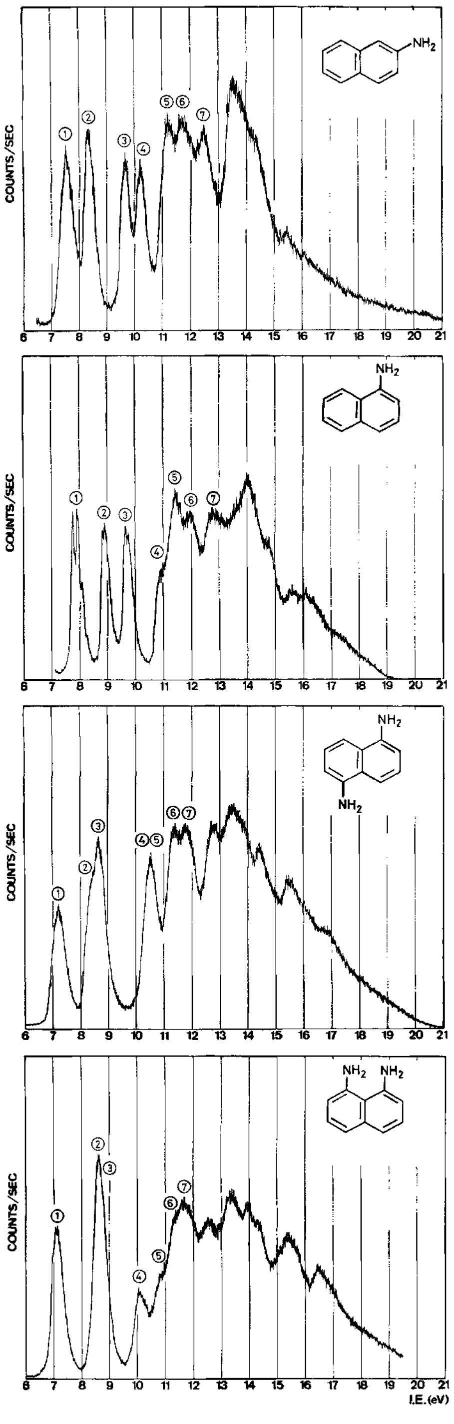
Compound	I_1	I_2	I_3	I_4	I_5	I_6	I_7
2	7.91 (7.74)	8.88 (8.68)	9.62 (9.42)	10.90 (10.60)	11.40	11.95	12.70
3	7.60 (7.10)	8.35	9.65 (9.30)	10.20	11.15	11.70	12.50
4	7.18 (6.74)	8.38 (7.96)	8.64	10.49	10.00[a]	11.35	11.80
5	7.10 (6.65)	8.60 (8.15)	8.80[b]	10.05 (9.65)	10.80	11.30	11.70
6	7.50 (7.00)	8.58 (8.20)	8.80[b]	9.94 (9.65)	11.00 (10.55)	11.25	11.70
7	7.20 (6.70)	7.98	8.50	8.80	9.80 (9.50)	10.60 (10.45)	11.10
8	7.05 (6.45)	7.47	8.49 (8.23)	9.05	9.80 (9.58)	10.60 (10.40)	11.20

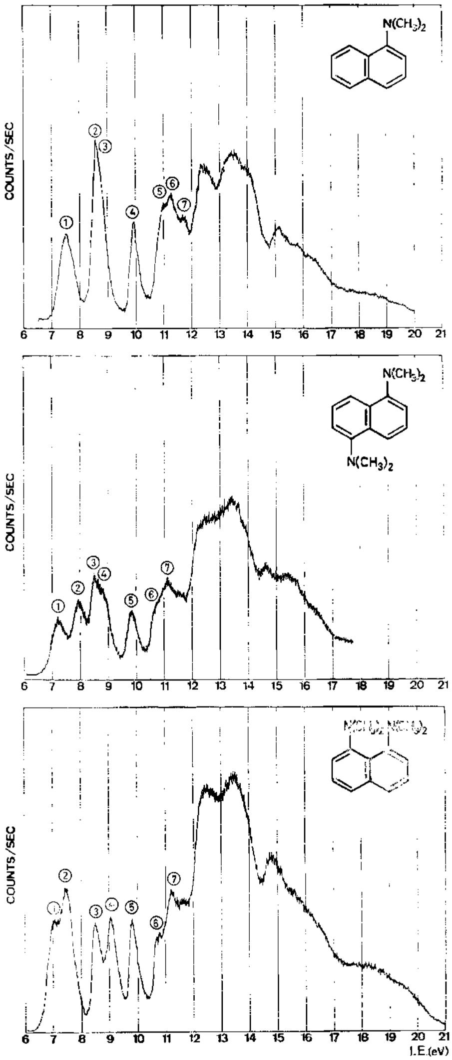
[a] Bands appear to overlap exactly.

[b] Estimated value from *Franck-Condon* profile of the overlapping bands.

As in the benzene derivatives, the spectral pattern is best discussed in relation to the PE. spectrum of the parent molecule. By comparison with the PE. spectra of naphthalene (**1**) [7], aminobenzenes [6] and ammonia [8] (first IE = 10.85 eV), all the bands below IE ≈ 11 eV are π-type or associated with the nitrogen lone-pair. In the spectra shown (Fig. 1 and 2) such a division is clearly seen and this facilitates the assignment. The bands following the first group show profuse overlap and clearcut identification is not unambiguous.

In all the spectra the bands have a broad *Frank-Condon* profile as is the case in the aminobenzenes [6]. This is ascribed to the combined effects of conformational flexibility, changes in geometry on ionization and to overlap of vibrational progressions excited. However, there is some evidence of vibrational fine structure on some of the π-bands. In the PE. spectrum of 1-amino-naphthalene (**2**) (Fig. 2) it is distinct on the





▲

Fig. 2. *He I photoelectron spectra of 1-dimethylaminonaphthalene* **6**, *1,5-bis(dimethylamino)naphthalene* **7** *and 1,8-bis(dimethylamino)naphthalene* **8**

◀ Fig. 1. *He I photoelectron spectra of* **2**-*aminonaphthalene* **3**, *1-aminonaphthalene* **2**, *1,5-diaminonaphthalene* **4** *and 1,8-diaminonaphthalene* **5**

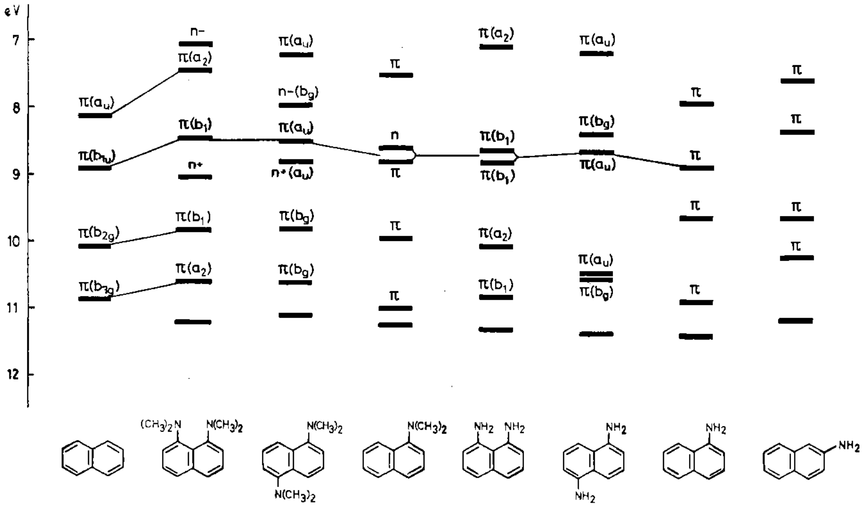
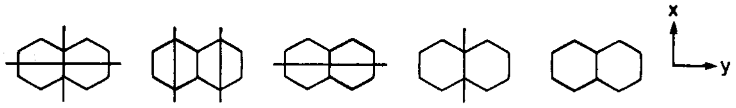


Fig. 3. *Correlation diagram of the energy levels of the aminonaphthalenes* **2–8**. The $\pi(b_{1u})$ band of naphthalene is correlated throughout the *peri*-derivates. For **8**, in the C_2 conformation (see text), the band labels are π(a), π(b), π(b), π(a), π(b) and π(a) respectively, with increase of IE.

first and third bands (1370 and 1000 cm^{-1} respectively) and albeit assignment to particular vibrational modes is not possible in view of the large choice possible (C_s symmetry), the frequencies are quite similar to those discernible on the first and third bands (1400 and 1200 cm^{-1} respectively) in the PE. spectrum of **1** [7–8].

Discussion. – The first group of bands (7–11 eV) are associated with electrons ejected from π and nitrogen lone-pair type orbitals. As these bands are separated from the sigma bands, and are sensitive to substituent and geometrical changes, they are of primary concern here.

The spectral pattern is advantageously discussed by considering the substituted naphthalenes as composite molecules, where the amino (or dimethyl-amino) fragment perturbs the naphthalene π-system. In Fig. 4 are represented the nodal properties of the five π-MO's of naphthalene, their symmetry designations (D_{2h} point group) and the corresponding IE's. The first three IE's are known with confidence from the PE. spectrum; however, some uncertainty exists about the precise value of the fifth and also, but to a lesser extent, of the fourth. With these as the starting point the perturba-



D_{2h}	a_u	b_{1u}	b_{2g}	b_{3g}	b_{1u}
I.E.(eV)	8.12	8.91	10.08	10.85	~12.5
ψ_j; j =	5	4	3	2	1

Fig. 4. *Characteristics of the five π-MOs of naphthalene*

tion of the substituent is separated, for convenience, into the inductive (first order) and conjugative (second order) contributions. The former is represented as the change in the *Coulomb* integral ($\delta\alpha$) as the result of replacement of the hydrogen by the substituent, while the latter, through a resonance integral B_{CX}. Such an approach is often utilised in the discussion of PE. spectra [9] and is briefly outlined.

For the 2p atomic orbital Φ_s of the π-system at the point of substitution s, and for Φ_t adjacent, the change in orbital energy ($\delta\varepsilon_J$) of the π-MO ψ_J, with respect to the unperturbed orbital energy ε_J is given by first order perturbation theory

$$\delta\varepsilon_J = \sum_s c_{Js}^2\,\delta\alpha + \sum_t c_{Jt}^2 \cdot m \cdot \delta\alpha \qquad (1)$$

where c_{Js} and c_{Jt} refer to the coefficients of Φ_s and Φ_t respectively in the ψ_J MO. The inductive parameter $\delta\alpha$ is defined by the perturbation operator **h**

$$\langle\Phi_s|\mathbf{h}|\Phi_s\rangle = \delta\alpha \text{ and } \langle\Phi_t|\mathbf{h}|\Phi_t\rangle = m \cdot \delta\alpha \qquad (2)$$

where

$$0 \leqslant m \leqslant 1. \qquad (3)$$

A value of $^1/_3$ is obtained for m from regression calculations based on the PE. data [10–11] in accord with the value used intuitively in the past by chemists.

The effect of conjugation is described by the resonance integral (B_{CX}) between the AO Φ_s and the atomic or group orbital of X, ψ_X, having the correct symmetry to interact

$$B_{CX} = \langle\psi_X|\mathbf{h}|\Phi_s\rangle. \qquad (4)$$

The basis energies, A_X, are defined by

$$A_X = \langle\psi_X|\mathbf{H}|\psi_X\rangle. \qquad (5)$$

To link the experimental vertical IE (I_J) to the orbital energy (ε_J) when electrons are ejected from the orbital ψ_J, *Koopmans'* theorem is invoked [12]:

$$\varepsilon_J = -I_J \qquad (6)$$

with awareness of the implications of this approximation. The eigenvalues (ε_i) of the LCMO model are obtained from the solution of the secular equations defined by (1), (4) and (5), and within the *Hückel* scheme.

If, for symmetry reasons, say the conjugative perturbation vanishes, (*e.g.* $c_{Js} = 0$) the parameter $\delta\alpha$ can be easily inferred. Such a case presents itself in substituted benzenes where the symmetry of the π-orbitals derived from the degenerate orbital pair of benzene, e_{1g}, (D_{6h} symmetry) is so favoured. Thus, this analysis of the π-IEs of aminobenzenes [6] [13] yields the average values $\delta\alpha$ ($N(CH_3)_2$) = 1.9 eV and $\delta\alpha(NH_2)$ = 0.5 eV, representing the inductive destabilization of the orbital energy (ε_J) when a hydrogen is replaced by the respective amino component.

In *peri*-substituted naphthalenes the coefficient of the Φ_s AO is zero for the HMO ψ_4 (Fig. 4) and hence the conjugative perturbation can be neglected. This enables a check to be made of the $\delta\alpha$ parameters directly. In **7** or **8**, the destabilization $\delta\varepsilon_4$ is thus evaluated by (1) to be 0.40 eV and the corresponding experimental changes (Tab. 1) are 0.41 eV and 0.42 eV (by (6)) respectively. In the amino derivatives **4** and **5**, the predicted destabilization is 0.05 eV per amino group in agreement with the small changes observed; quantitatively, this is not significant in view of the broadness and overlap of this band (Fig. 1).

The parameters A_X and B_{CX}, defined by (5) and (4) respectively, are obtained from the previous analyses of the PE. spectra of the amino [6] and diamino benzenes [13]:

$$A_{N(CH_3)_2} = -8.7\text{ eV} \qquad A_{NH_2} = -10.6\text{ eV} \qquad B_{CN} = -2.4\text{ eV} \tag{7}$$

These values produce consistent representation in all the amino derivatives studied. For instance, the destabilization of the basis energy of the nitrogen lone-pair (A_X) by 0.2 eV with respect to the corresponding energy of the lone-pair in $NH(CH_3)_2$ (–8.93 eV) and NH_3 (–10.80 eV) for $N(CH_3)_2$ and NH_2 groups respectively is in accord with the change observed on replacement of a hydrogen by an sp^2 carbon atom [9].

Dimethylamino naphthalenes. – The basis energy values $\varepsilon_J' = \varepsilon_J + \delta\varepsilon_J$ for the perturbed π-MO's of the naphthalene fragment for **7** and **8** are obtained by application of (1), the IE's listed in Fig. 4 and using the standard *Hückel* coefficients, c_{Js} and c_{Jt}, for **1**

$$\varepsilon_J'\ (\text{eV}):\ -7.40\ -8.50\ -9.35\ -10.40\ -11.9$$

By comparison (*via* (6)) with the PE. spectrum of **8** these values agree with the IEs of the following bands: ②, ③, ⑤ and ⑥.

This can also be seen from the correlation diagram (Fig. 3). This would suggest that the overlap between the nitrogen lone-pairs (n_j j = a, b) and the Φ_s orbitals is small as the effect of any residual conjugation is not significant on the energies ε_J' for dihedral angle (θ) (between the axes of n_j and Φ_s orbitals) in the range of 70 to 90°.

The two remaining bands ① and ④ in the first group in the PE. spectrum of **8** would have to be correlated with electrons which stem from orbitals of the nitrogen lone-pairs or, more correctly, with orbitals to which the symmetry adapted linear combinations

$$\begin{aligned} n_- &= 1/\sqrt{2}\,(n_a - n_b) \\ n_+ &= 1/\sqrt{2}\,(n_a + n_b) \end{aligned} \tag{8}$$

make the major contributions.

The splitting (ΔE) between bands ① and ④ of 2.0 eV then represents the magnitude of the interactions, classified nowadays as *through-space*, here σ-σ type overlap of the lone-pairs, and *through-bond* [14] with deeper lying σ-orbitals of correct symmetry. In the PE. spectra of hydrazines [15–17] where *through-space* interaction (π-π overlap of the nitrogen lone-pairs) dominates when geometrical constrains are imposed so that the dihedral angle θ is close to zero, the splitting of the bands associated with the linear combinations as designated in (8) is found to be $\approx$ 1.8 eV [17]. From the ratio of *Slater* overlap integrals for sp^3 hybrids of the nitrogen lone-pairs at the internuclear distances of 1.45 Å for the hydrazine (π-π overlap), and at 2.44 Å for **8** (σ-σ overlap), it seems that the magnitude of the *through-space* interaction should be appreciably smaller in the latter.

Then it is likely that *through-bond* delocalizations are important in reinforcing the *through-space* sequence of n_- above n_+. This is also suggested from comparison of the mean of the IE's of these bands, 8.05 eV, with for example the IE of the lone-pair of $(CH_3)_3N$, 8.45 eV [6]. This destabilization can be attributed to interactions with the deeper lying σ-levels and is consistent with the results of calculations [18], which show that the symmetry sequence of the highest occupied σ-orbitals of the naphthalene framework would retain the *through-space* sequence.

The present discussion of the PE. spectrum of **8** refers strictly to the vapour phase and the distortions will differ to some extent depending on the physical state of the molecule (*cf.* biphenyl [4]). However, a dihedral angle $\theta = 60$–$70°$ has been deduced for the liquid phase from an ESR. study of the anion [19], and the angle suggested by UV. and NMR. data [2] is 30–40°. The recent X-ray crystallographic analysis [20] of **8** is also consistent with a dihedral angle of about 40° and a C_2 molecular point group. The distance between the nitrogens is 2.79 Å and the naphthalene ring is non-planar.

For a dihedral angle of 40° the perturbation due to direct overlap between the amino lonepairs (s) and the π-system has to be included by (4). For deviations from coplanarity as result of angular twisting around the interannular (C-N) bond, the non-zero off-diagonal elements (4) may be approximated by

$$B_{CN}(\theta) = B_{CN}(0)\cos\theta \tag{9}$$

The spectral pattern can then be reasonably reproduced with $\theta = 40°$. For the a irreducible representations

ε_i (eV):	—6.74	—9.08	—10.69
IE (eV):	7.05 ①	9.05 ④	10.60 ⑥

and for the b irreducible representations

ε_i (eV):	—7.80	—8.50	—9.95	—12.12
IE (eV):	7.47 ②	8.49 ③	9.80 ⑤	~12.3

In this case, the lone-pairs are delocalised and the eigenvectors to which the linear combinations n_+ and n_- (8) contribute most are associated with the fourth and second bands respectively. In view of the two possible interpretations, further vapour phase structure studies are desirable.

For **6** a satisfactory agreement between the experimental IE's and the calculated eigenvalues (ε_i) is obtained for $B_{CN}(\theta)$ corresponding to θ value in the vicinity of 60°, e.g. $\theta = 60°$:

ε_i (eV):	– 7.50	– 8.65	– 8.70	– 9.80	– 10.66	– 12.24
IE (eV):	7.50	8.58	8.80	9.94	11.0	12.3

The comparison is intended primarily for the bands below IE $\approx$ 11 eV where π-σ interactions are minimized (*vide infra*); the other values are given for the sake of completeness. The eigenvectors corresponding to the above eigenvalues, ε_i indicate that band ② is associated with the orbital which has the largest contribution from the nitrogen lone-pair basis (n).

In the *peri*-disubstituted derivatives the solution for the eigenvalues may be simplified through symmetry. This is advantageous in that two independent comparisons can be made. For **7** (with C_{2h} symmetry) the determinant of the b_g irreducible representations yields eigenvalues which reproduce the spectral pattern reasonably for $\theta = 50$–$60°$, *e.g.* $\theta = 56°$:

ε_i (eV):	-8.09	-9.68	-10.57
IE (eV):	7.98 ②	9.80 ⑤	10.60 ⑥

while the a_u determinant yields the following comparison for $\theta = 56°$:

ε_i (eV):	-7.00	-8.50	-8.99	-12.0
IE (eV):	7.20 ①	8.50 ③	8.80 ④	–

These values are in good agreement in view of the simplicity of the approach and the experimental uncertainties. The eigenvectors show that bands ② and ④ are associated with the orbitals to which the linear combinations n_- and n_+ (8) respectively, make the largest contributions. However, it should be borne in mind that although the energies may be satisfactory the eigenvectors themselves may be in error [21].

The preceeding analysis of **6** and **7** suggests that the consequence of the steric strain due to *peri* interactions is, in part, angular rotation of the dimethylamino group(s) ($\theta \approx 60°$). This is as expected from *Van der Waals'* radii of the *peri*-substituents which suggest that $\theta \geqslant 45°$. In solution the experimental evidence of reaction rates [1] [22] and dissociation constants [2] [23] also indicates qualitatively some similar distortion.

Aminonaphthalenes. – The PE. spectra of **2** and **3**, **4** and **5** (Fig. 2), also show differences in the pattern of the first group of bands. Proceeding to interpret the variation by the perturbation approach used, the following comparison is obtained for **3**:

ε_i (eV):	-7.76	-8.43	-9.80	-10.21	-11.74	-12.70
IE (eV):	7.60	8.35	9.65	10.20	11.70	12.50

corresponding to zero dihedral angle as in aniline [6]. In contrast, with the three *peri*-amino naphthalenes **2**, **4** and **5** less satisfactory quantitative agreement is achieved. As the basis of the amino group ($A_{NH_2} = -10.6$) is now much closer in energy to the σ-levels than was the dimethylamino group ($A_{N(CH_3)_2} = -8.70$), it is not unexpected that the implicit neglect of π-σ interactions is no longer a reasonable approximation when the latter can occur. Therefore, the semi-quantitative analysis which was possible for the *peri*-dimethylamino naphthalenes is not attempted. Nevertheless, the relative order of the assignments for the first group of bands, summarised in Fig. 4, is not altered.

Application of this treatment to the PE. spectra of 1- and 2-methoxy naphthalenes [24] with parameters obtained from the PE. spectra of the methoxy benzenes [6] [24],

$$A_{OCH_3} = -10.25 \text{ eV} \qquad B_{CO} = -2.2 \text{ eV and } \delta\alpha\,(OCH_3) = 0$$

gives good agreement with the first three bands for zero dihedral angles:

	1-Methoxynaphthalene			*2-Methoxynaphthalene*		
ε_i (eV):	–7.70	–8.91	–9.41	–7.86	–8.52	–9.82
IE (eV):	7.72	8.79	9.50	7.87	8.50	9.81

Thus, the discrepancies obtained with **2**, **4** and **5** can perhaps be taken as a qualitative indication of angular distortions. The difference between **2** and **3** agrees with the proximity of the *peri*-, as compared to the *ortho*-hydrogen [1]. Other evidence is conflicting however. Theoretical analysis predicts a dihedral angle of zero for both the species [25]. In the liquid, dissociation constants [23] and IR. data [1] suggest that the amino is twisted somewhat only in the *peri*-position, while molecular polarisability measurements were interpreted as $\theta \approx 28°$ for both [26].

In **5**, angular distortions are also suggested by calculations [19] which predict an energy minimum for $\theta \approx 30°$. In addition, with the amino groups in adjacent *peri*-positions, non-nearest neighbour interactions between the nitrogen should be considered. Indeed the first IE of **5**, 7.10 eV, is smaller than that of **4**, 7.18 eV, which is the reverse trend one would anticipate from the interaction terms for the same value of $B_{CN}(\theta)$, due to the different symmetry properties. As the NH_2 groups are probably more angularly twisted in **8** than in **4**, this difference in the first IEs can be attributed to the nitrogen lone-pairs interaction (c.f. **8**), absent in the 1,5 derivative, although π-σ interactions will also contribute. Accordingly, the higher $pK_a = 4.61$ of **5** [2] as compared to 4.07 of **4** [27] perhaps reflects that some relief of non-bonded interactions is again achieved on protonation.

Experimental. – The spectra were obtained with two different PE. spectrometers, both incorporating a $\pi/\sqrt{2}$ sector electrostatic cylindrical condenser analyser (10 cm radius) as described by *Turner* [28]. The PE. spectra of some of the samples were recorded on both instruments as a check for consistency for possible sample region surface charging phenomena. The former instrument was the one described by *Turner* [28], with modifications [4], while the other was based on the same design and built in the present laboratory. He I (and He II) resonance lines were utilised for the source of excitation. The experimental working resolution was 0.02–0.03 eV, full width at half-height for 5 eV electrons in all cases. The ionisation energies were determined by an *in situ* calibration with the rare gases. The data were reproducible to ± 0.02 eV. The samples were commercial products; 1,8-bis(dimethylamino)naphthalene was an *Aldrich Co.* product of tradename 'proton-sponge'. 1,5-bis(dimethylamino)-naphthalene was prepared from the corresponding amine [22] and purified by standard techniques. All the samples (solids) were sublimed prior to use and were inserted directly in the vicinity of the ionisation region which was heated to 60–150° to increase the sample vapour pressure.

I wish to thank Dr. *D. W. Turner*, Physical Chemistry Laboratory, Oxford, for the use of instruments and the *Royal Society* for a Research Fellowship.

This work is part 65 of project No. 2.823.73 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*; part 64 see ref. [29]. Financial support by *Ciba-Geigy S.A.*, *F. Hoffmann-La Roche & Cie. S.A.* and *Sandoz S.A.* is gratefully acknowledged.

I wish to thank Dr. *R. W. Alder* for drawing to my attention that an alternative interpretation of the PE. spectrum of 1,8-bis(dimethylamino)naphthalene is possible in accordance with the X-ray analysis and for a sample which instigated this work.

REFERENCES

[1] *V. Balasubramaniyan*, Chem. Rev. *66*, 567 (1966).
[2] *R. W. Adler, P. S. Bowman, W. R. S. Steele & D. R. Winterman*, Chem. Commun. *1968*, 723.

[3] See for example: *E. Heilbronner, J. P. Maier & E. Haselbach,* in 'Physical Methods in Heterocyclic Chemistry', edit. *A. Katritzky,* Academic Press, in print, for discussion and leading references.
[4] *J. P. Maier & D. W. Turner,* Disc. Faraday Soc. *54,* 149 (1972).
[5] *J. P. Maier & D. W. Turner,* J. C. S. Faraday II, *69,* 196 (1973).
[6] *J. P. Maier & D. W. Turner,* J. C. S. Faraday II, *69,* 521 (1973).
[7] *J. H. D. Eland & C. J. Danby,* Z. Naturforsch. *23a,* 355 (1968).
[8] *D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle,* 'Molecular Photoelectron Spectroscopy', Wiley, London, 1970.
[9] *E. Heilbronner,* XXIIIrd International Congress of Pure and Applied Chemistry, *7,* 9 (1971) and references given therein.
[10] *E. Heilbronner, V. Hornung, F. H. Pinkerton & S. F. Thames,* Helv. *55,* 289 (1972).
[11] *F. Brogli, E. Heilbronner & T. Kobayashi,* Helv. *55,* 274 (1972).
[12] *T. Koopmans,* Physica *1,* 104 (1934).
[13] *D. G. Streets, W. E. Hall & G. P. Ceasar,* Chem. Phys. Letters *17,* 90 (1972).
[14] *R. Hoffmann,* Acc. Chem. Research *4,* 1 (1971).
[15] *S. F. Nelsen, J. M. Buschek,* J. Amer. chem. Soc. *95,* 2011 (1973); *S. F. Nelsen, J. M. Buschek & D. J. Hinz,* ibid. *95,* 2013 (1973).
[16] *E. Haselbach, A. Mannschreck & W. Seitz,* Helv. *56,* 1614 (1973).
[17] *P. Rademacher,* Angew. Chem. *85,* 447 (1973).
[18] *R. E. Christoffersen,* J. Amer. chem. Soc. *93,* 4104 (1971), and references therein.
[19] *F. Gerson, E. Haselbach & G. Plattner,* Chem. Phys. Letters *12,* 316 (1971).
[20] *E. Einspahr, J. B. Robert, R. E. Marsh & J. D. Roberts,* Acta. Cryst. *29B,* 1611 (1973).
[21] *E. Heilbronner, V. Hornung, J. P. Maier & E. Kloster-Jensen,* J. Amer. chem. Soc., in print.
[22] *A. Zweig, A. H. Maurer & R. G. Roberts,* J. Org. Chemistry *32,* 1322 (1967).
[23] *A. Fisher, G. J. Sutherland, R. D. Topsom & J. Vaughan,* J. chem. Soc. *1965,* 5948.
[24] *H. Bock, G. Wagner & J. Kroner,* Chem. Ber. *105,* 3850 (1972).
[25] *K. Sekigawa,* Tetrahedron *26,* 5395 (1970).
[26] *R. J. W. LeFèvre & A. Sundaraum,* J. chem. Soc. *1962,* 4756.
[27] *A. Bryson,* J. Amer. chem. Soc. *82,* 4862 (1960).
[28] *D. W. Turner,* Proc. Roy. Soc. *A307,* 15 (1968).
[29] *H. D. Martin, C. Heller, E. Haselbach, Z. Lanyiova,* Helv. *57,* 465 (1974).

---

109. 3-*C*-Hydroxymethyl-D-riburonic Acid Synthesis of the Branched-Chain Uronic Acid and Comparison with a Carbohydrate Component of a Naturally Occurring Bilirubin Conjugate

by **Walter P. Blackstock, Clive C. Kuenzle**[1] and **Conrad H. Eugster**

Institute of Organic Chemistry, University of Zürich,
Rämistrasse 76, CH–8001 Zürich (Switzerland)

(22. III. 74)

Summary. A novel carbohydrate has previously been isolated from human bile as a complex glycoside of bilirubin [1]. This compound has been tentatively identified as 3-*C*-hydroxymethyl-D-riburonic acid. To test this structural assignment the proposed branched-chain uronic acid was synthesized. Gas chromatographic and mass spectrometric comparison of the natural and synthetic

---

[1] Present address: Department of Pharmacology and Biochemistry, School of Vet. Medicine, University of Zürich, Winterthurerstrasse 260, CH–8057 Zürich (Switzerland).