197. 'Lone Pair' and 'CI Bond' Ionization Energies of *exo*- and *endo*-2-Norbornyl Iodides

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Summary

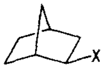
A PE-spectroscopic study of *exo*- and *endo*-2-norbornyl iodides suggests that the relative ability of the 2-norbornyl group to stabilize an electron deficiency on a substituent X (*e.g.* I) in *exo*- or *endo*-position depends on the location of the positive charge. There is *no* difference if the positive hole is strongly localized *on* the substituent X (*e.g.* the $5p^{-1}$ state of the title compounds). On the other hand, our results indicate that a positive hole semi-localized *in* an *exo*-C–X bond is better stabilized by the 2-norbornyl group than a semi-localized, positive hole in an *endo*-C–X bond.

Introduction. – The question, whether there is a significant difference in the ability of the 2-norbornyl group (NB) to stabilize an electron deficiency in a substituent X located in the *exo*- (**1**) or the *endo*-(**2**) position, is of obvious interest in connection with the protracted discussion concerning the widely different rates of formation of the NB cation from epimeric NB derivatives **1** and **2** [1].

In the former case, the ability of the NB moiety to stabilize a positive charge *on* a 2-*exo*- or a 2-*endo*-substituent has been shown to differ slightly, if at all, when the measurement is carried out in solution. From the rates of solvolysis of *p*-alkyl(*tert*-cumyl) chlorides, *Brown et al.* [2] derived, σ^+ substituent constants for the *p-exo*- and *p-endo*-NB groups, which differ only marginally: σ^+(*exo*-NB) = –0.309; σ^+(*endo*-NB) = –0.295. (For comparison: σ^+(isopropyl) = –0.280; σ^+(cyclopentyl) = –0.302; σ^+(cyclopropyl) = –0.462.) In a similar vein, NMR investigations by *Menger & Thamos* [3], of *exo*- and *endo*-2-(dimethylamino)norbornanes (**1**, **2**; X = $N(CH_3)_2$) did not reveal substantial differences in the rates of NH proton exchange, nitrogen inversion or amine quaternization.

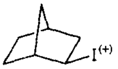
Photoelectron (PE) spectroscopy being an obvious tool for the investigation of such questions, *Nugent et al.* [4] measured the PE spectra of the (2-norbornyl)methyl mercury epimers (**1**, **2**; X = $HgCH_3$). They found that the first ionization energy of the *exo*-isomer (I_1^m = 8.28 eV) is 0.2 eV smaller than that of the *endo*-isomer (I_1^m = 8.47

eV). (For comparison: I_1^m(dimethylmercury) = 9.33 eV, I_1^m ((*tert*-butyl)methyl mercury) = 8.31 eV [5]). From this they concluded that the NB group stabilizes a positive charge more efficiently from the *exo*- than the *endo*-position, seemingly in conflict with the results reported in [2] [3]. However, for reasons to be discussed below, and to which the above authors had already drawn attention [5], the group $X = HgCH_3$ is not the best choice for this type of experiment.

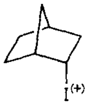


1

2



3$^{(+)}$



4$^{(+)}$

It seemed, therefore, of interest to check the above results by measuring the ionization energy of a target group X in both **1** and **2**, making the experiment as sensitive as possible. To this end, X should satisfy the following conditions: *1*) The highest occupied molecular orbital φ_{HOMO} of **1** and **2** should be strongly localized on X so that the positive hole of the ground state radical cations **1**$^+$ and **2**$^+$ is concentrated as much as possible on the X moiety. *2*) The basis orbitals ϕ_j of X which contribute to φ_{HOMO} should exhibit an orbital energy A_j as close as possible to, but slightly above, the energy of the highest occupied orbitals of the σ-manifold of the NB group. This would ensure that the influence of the latter group on the ionization energy of X is practically first-order, providing an optimal opportunity to discriminate between the charge stabilizing effects of the NB group in **1**$^+$ and **2**$^+$. Note, however, that this condition is necessarily incompatible with the previous requirement of a strong localization of φ_{HOMO} on X, so that we have to strike a judicious compromise. *3*) The C–X σ-bond orbital λ_{CX} should not interfere with φ_{HOMO}, to allow a clean separation of the expected effects. On the other hand it would be of advantage, if the PE band corresponding to electron ejection from a molecular orbital with strong λ_{CX} participation could be observed. *4*) Finally, X should be such that the PE band corresponding to φ_{HOMO}^{-1} is sharp so that its position I_1^m can be measured with sufficient accuracy.

From previous experience [6] [7] it is obvious that X = I is the target of choice. A further advantage of choosing I, is that the I atom has a large spin-orbit coupling coefficient ζ_{SOC} [8] which provides an additional criterion for the I/NB interaction in the radical cations **3**$^+$ and **4**$^+$.

Experimental Results. – Accordingly, the two epimeric NB-iodides **3** and **4** were synthesized [9] and their PE spectra recorded (*cf. Fig. 1*). The following results are immediately obvious: *1*) The first two bands ①, ② in the PE spectra of **3** and **4** correspond to the ejection of an electron from what is essentially an I 5p lone-pair orbital. If the situation at the I-site were axially symmetrical, the states of **3**$^+$ and **4**$^+$ corresponding to bands ① and ② could be labeled $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, respectively, their split $\Delta_{SOC} = I_2^m - I_1^m$ being due only to spin-orbit coupling. The mean position of the two bands ①, ② $\overline{I_{1,2}^m} = (I_1^m + I_2^m)/2$, *i.e.* corresponding to $^2\Pi$ corrected for spin-orbit coupling, is exactly the same for both epimers, namely $\overline{I_{1,2}^m} = 9.26$ eV, within experimental error. *2*) In addition, the split $I_2^m - I_1^m = 0.52$ eV is also the same in the PE spectra of **3** and **4**, within ±0.01 eV. *3*) The width at half height ($w_{1/2}$) of the first two bands are $w_{1/2}$ ① ≈ 0.2 eV, $w_{1/2}$ ② ≈ 0.2_5 eV for **3** and $w_{1/2}$ ① ≈ 0.1 eV, $w_{1/2}$ ② ≈ 0.2 eV for **4**, *i.e.* marginally broader for **3**. *4*) The third maximum ③ in the PE spectra of **3** and **4** is due to the ejection of an electron from a molecular orbital dominated by the C–I bond σ-orbital (*cf.* below). The position of this band is $I_3^m = 10.3_5$ eV for **3** and $I_3^m = 10.5_5$ eV for **4**, both values being affected with errors of ± 0.05 to ±0.10 eV, because of the broadness of the bands and because they are overlapped by other bands of the NB manifold (*cf.* the PE spectrum of norbornane [10]).

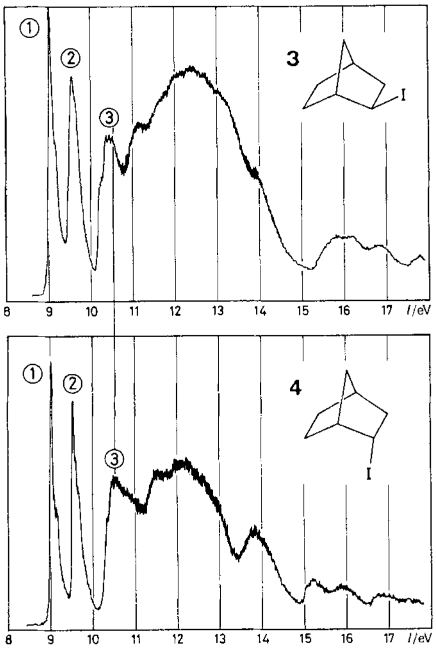


Fig. 1. *He(Iα) PE spectra of* exo- *and* endo-*2-norbornyl iodides*

	I^m_1/eV	I^m_2/eV	I^m_3/eV
3	9.00	9.52	10.3_5
4	9.00	9.52	10.5_5

The 'Lone Pair' Ionization Energy. – From the fact that the difference between the mean ionization energies $\overline{I^m_{1,2}}$ of **3** and **4** is less than ~ 0.01 eV we deduce that the ionization energy reducing effect of the NB group (whatever its electronic mechanism) is (almost) independent of the local configuration of the C–I bond in position 2. The significance of this result can only be assessed by comparison with the PE data of other alkyl iodides [7] [11].

Following the example of *Cocksey, Eland & Danby* [12], we have derived some time ago [13] a set of *Hammett*-type substituent constants $\mu^H(R)$, which are defined as the difference

$$\mu^H(R) = \overline{I^m_{1,2}}(RI) - \overline{I^m_{1,2}}(HI) \qquad (1)$$

between the mean ionization energies (*i.e.* corrected for spin-orbit coupling) of the $5p^{-1}$ bands in the PE spectra of the RI and HI. It has been shown [13] that the constants $\mu^H(R)$ yield an excellent linear regression with the traditional *Taft* $\sigma^*(R)$ values (correlation coefficient $r = 0.9883$):

$$\frac{\mu^H(R)}{eV} = -0.92 + 1.82\,\sigma^*(R) \qquad (2)$$

Accordingly, the observation that the mean ionization energies $\overline{I^m_{1,2}}$ of the two epimers **3** and **4** differ by less than ~ 0.01 eV means that the σ^*(NB) value is the same within ± 0.005σ^* units in both $\mathbf{3}^+$ and $\mathbf{4}^+$. Presumably this will be true for other groups X in **1** and **2**, at least within the conditions prevailing in **3** and **4**.

From $\overline{I^m_{1,2}} = 9.26$ eV for **3** and **4**, together with $\overline{I^m_{1,2}} = 10.72$ eV for HI, we obtain according to (*1*) μ^H(NB) = −1.46 eV for both epimers. Regression (*2*) yields σ^*(NB) = −0.30, which happens to be the same as for R = *t*-Bu. (Note that the latter group yields μ^H(*t*-Bu) = −1.36, *i.e.* slightly less than μ^H(NB) = −1.46, but that the corresponding point does not lie exactly on the regression line.) Because of the convention σ^*(Me) = 0 one has σ^*(H) = 0.49, and therefore an effective shift due to the NB group of σ^*(NB)−σ^*(H) = −0.79. Thus the difference between the $5p^{-1}$ ionization energy reducing effects of NB in the two epimers **3** and **4** is less than 1%, and this holds presumably for other epimeric compounds **1**, **2**.

The competition between spin-orbit coupling and conjugation in alkyl halides [11] or in haloacetylenes [14] and its repercussion on their PE spectra has been studied in detail. In a first approximation, the size of the spin-orbit coupling split Δ_{SOC} is a measure of the positive charge on the halogen atom for a given state of the radical cation (*e.g.* $\mathbf{3}^+$, $\mathbf{4}^+$) and thus of the coefficients of the halogen basis orbitals in the corresponding linear combination describing the vacated molecular orbital (*e.g.* the coefficients of the 5p I atomic orbitals in the φ_{HOMO} linear combination). A full charge on the bound I atom would lead to $\Delta_{SOC} \approx \zeta(I) = 0.63$ eV, *i.e.* equal to the spin-orbit coupling parameter. It has been observed [11] that for RI, Δ_{SOC} decreases with increasing size of R, *e.g.* Δ_{SOC}(MeI) = 0.62 eV, Δ_{SOC}(*t*-BuI) = 0.56 eV, *i.e.* with increasing delocalization of the positive hole into the alkyl moiety. This agrees nicely with the value $\Delta_{SOC} = 0.52$ eV for **3** and **4** if we remember that both **3** and **4** are a little easier to ionize than *t*-BuI.

The 'CI Bond' Ionization Energy. – We now turn our attention to bands ③ in the PE spectra of **3** and **4** which are found at $I^m_3 = 10.3_5$ eV and $I^m_3 = 10.5_5$ eV, respectively. There is no doubt that the third band in the PE spectra of the usual alkyl iodides RI,

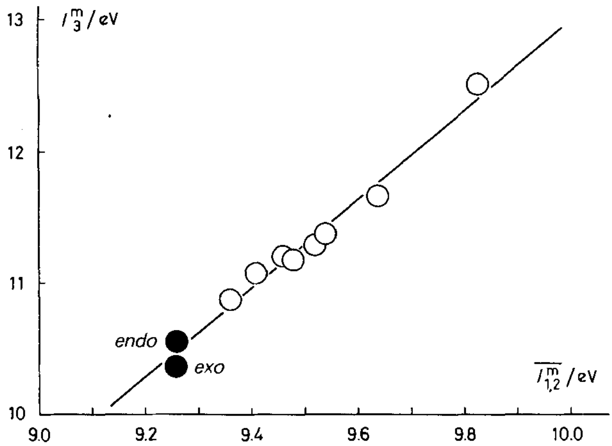


Fig. 2. *Linear regression* (3) *of* I^m_3 *on* $\overline{I^m_{1,2}}$ *for* RI (R = Me, Et, Pr, i-Pr, Bu, i-Bu, *s*-Bu, *t*-Bu, *cf.* [13]), *and for* **3** *and* **4**

with R = H to *t*-Bu is due to the ejection from an orbital which can be described as the C–I σ-orbital mixed extensively with appropriate R-group orbitals [7]. Furthermore, it is observed, as shown in *Fig. 2,* that the corresponding ionization energy I_3^m correlates linearly with $\overline{I_{1,2}^m}$, according to the regression:

$$(I_3^m/\text{eV}) = (11.39 \pm 0.03) + (3.35 \pm 0.22)[(\overline{I_{1,2}^m}/\text{eV}) - 9.53] \qquad (3)$$

The limits given for the coefficients of (*3*) are standard errors. Note that the confidence limits (90% security level) for I_3^m of HI derived from $\overline{I_{1,2}^m}$(HI) = 10.72 eV delimit the range from 14.85 to 15.91 eV, and that they do not encompass the observed value I_3^m(HI) = 14.25 eV, as was to be expected because of the different type of σ-orbital. Extrapolation of (*3*) to the value $\overline{I_{1,2}^m} = 9.26$ eV for **3** and **4** yields the 90% security confidence limits of 10.28 to 10.70 eV for I_3^m, as compared to the experimental values 10.3_5 eV and 10.5_5 eV for **3** and **4**, respectively. Accordingly, we assign bands ③ in the PE spectra of **3** and **4** to a $\sigma(\text{C–I})^{-1}$ dominated state. Although the I_3^m values of **3** and **4** differ by 0.2 eV it is obviously impossible to tell which of the two is more on line with the corresponding values of the usual series of RI. This is evident from the graphical representation of regression (*3*) shown in *Fig. 2.*

Notwithstanding the fact that we can not determine which of the two compounds **3**, **4** is the 'odd-man-out', the difference between the ionization energies $I_3^m(\mathbf{4}) - I_3^m(\mathbf{3}) = 0.2$ eV is significant and we can safely conclude that the NB group stabilizes a positive charge (semi)localized in an *exo*-C–X σ-bond better than that (semi)localized in an *endo*-C–X σ-bond. This result is in complete qualitative and quantitative agreement with the conclusions of *Nugent et al.* [4], mentioned in the *Introduction.*

Discussion. – The absence or presence of a configuration dependence of the positive charge stabilizing effect of the NB group depends on the type of (semi)localization of the positive hole: *a*) If the positive hole is (semi)localized on the centre X, being due to electron ejection from an orbital centred on X and essentially orthogonal to the C–X σ-bond orbital (*e.g.* the 5p orbitals in **3** or **4**) then the charge stabilizing effect of the NB group is independent of whether X is in *endo*- or *exo*-position. In addition, this effect does not differ significantly in size from that observed for comparable alkyl groups *e.g.* a *t*-Bu or cyclohexyl group. *b*) If the positive hole is (semi)localized on the C–X σ-bond, being due to electron ejection from an orbital centred on this bond (*e.g.* the (I σ-orbitals in **3** or **4**), then the charge stabilizing effect of the NB group is larger if the C–X bond occupies the *exo*-, rather than the *endo*-position. However, the size of both effects does not differ significantly from what is expected on the basis of other 'normal' RX compounds, as shown in *Fig. 2.* Compared to the stabilizing effect discussed under *a*, the latter effect is larger by a factor of 3.3 (*cf.* regression (*3*)).

Crudely speaking one could say that the configuration dependence of the charge stabilizing effect of a NB group depends on the distance between the positive hole and centre C(2), although the true reason is clearly not simply a question of distance, but rather of the local symmetry and/or orthogonality of the orbitals involved. It now becomes obvious that the conclusions reached on the one hand by *e.g. Brown et al.* [2] or *Menger & Thamos* [3], and on the other by *Nugent et al.* [4] do not contradict each other. The former [2] [3] refer to case *a* (no conformation dependence) whereas the latter belong to case *b* (conformation dependent). *Jorgensen & Munroe* [15] have carried out MINDO/3 calculations for the 2-norbornyl chlorides (**1**, **2**; X = Cl). According to their results the first ionization energies should differ by only 0.07 eV (I_1^{calc}(**1**, Cl) = 10.22 eV, I_1^{calc}(**2**, Cl) = 10.29 eV). An anlogous theoretical analysis of the electronic structure of **3** and **4**, using semi-empirical or other quantum chemical methods is hampered by the lack of reliable basis energies for the heavy I atom. However, we have shown [6] that a recently proposed equivalent bond orbital model [16] can be heuristically useful for the interpretation of the PE spectra of halogen substituted norbornanes. Applying this model (described in detail in [6]) to **3** and **4** (with and without inclusion of spin-orbit coupling [11]) yields the results summarized in the *Table*. They allow a rough estimate of the relative amounts of mixing between either the 5pAO on the I atom or the λ_{CI} localized molecular orbital with the σ orbitals of the NB moiety. Whereas the φ_{HOMO} and $\varphi_{HOMO\text{-}1}$ (associated with bands ① and ②) are characterized by a 5p participation of ~ 60 to 70%, the orbital $\varphi_{HOMO\text{-}2}$ corresponding to band ③ possesses only ~ 40% λ_{CI} character. As this relationship is also the one typical for other RI, it is obvious that the position of band ③ is much more sensitive to changes in R than the positions of bands ① and ②. From the *Table* we see that $\overline{I_{1,2}^{m}}$(calc) is 9.33 eV for **3** and 9.22 for **4**, *i.e.* practically the same within the limits of error imposed by our model, whereas I_3^m(calc) is found to be 10.09 eV for **3** and 10.60 eV for **4**, in reasonable accord with observation.

Table. *EBO Model Orbital Energies ε_j and Percent Contribution of the Localized Basis Orbitals 5p and λ_{CI}.* The model and the parameters used are described in [17]. The percentages of the 5p and the λ_{CI} contributions are defined as $100 \cdot c_{\mu j}^2$, where $c_{\mu j}$ is the coefficient of 5p or λ_{CI} in the linear combination φ_j belonging to ε_j. SOC = Spin Orbit Coupling.

exo-2-Norbornyl iodide (**3**)						*endo*-2-Norbornyl iodide (**4**)					
without SOC			SOC included			without SOC			SOC included		
$-\varepsilon_j$/eV	5p	λ_{CI}	$-\varepsilon_j$/eV	5p	λ_{CI}	$-\varepsilon_j$/eV	5p	λ_{CI}	$-\varepsilon_j$/eV	5p	λ_{CI}
9.22	60	–	9.11	67	–	9.18	55	–	9.03	63	–
9.45	67	2	9.56	59	2	9.26	61	–	9.40	53	–
10.08	5	42	10.09	6	42	10.60	3	39	10.60	3	39
10.97	4	9	10.97	4	8	10.82	10	18	10.82	10	18
11.26	2	–	11.25	2	1	11.22	10	–	11.23	10	–

According to the *Table* the mean percentage contribution of the I 5p atomic orbitals to φ_{HOMO} and $\varphi_{HOMO\text{-}1}$ is 64% in **3**, but only 56% in **4**. This agrees qualitatively with the observation that the $w_{1/2}$ values of bands ① ② are larger in the PE spectrum of **3** than that of **4**, *i.e.* that orbital mixing is larger in the former compound. As explained in detail in [11], such a difference in orbital mixing does not necessarily reflect in the spin-orbit coupling split.

It is, of course, an open question if the above conclusions can be extrapolated to other groups X in **1** and **2**. However, we believe this to be the case, as long as the localized valence shell orbitals of X do not differ too drastically in symmetry and nodal properties from those of an I atom.

The main advantage of the present PE investigation over the previous one, which used X = $HgCH_3$ as a target [4], resides in the fact that both situations *a* and *b* mentioned above are covered within the same molecule, thus providing an internal calibration.

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