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# Intramolecular Interactions and Hindered Rotation in Tropinone Urethanes: A Combined PE-, ET- and DNMR-Spectroscopic Study[1)]

*Hans-Dieter Martin**[a], *Monika Müller*[a], *Bernhard Mayer*[a], *Hatim Haddad*[a], *Alois Steigel*[a], *Guiseppe Distefano*[b], and *Alberto Modelli*[c]

Institut für Organische Chemie I, Universität Düsseldorf[a], Universitätsstr. 1, D-4000 Düsseldorf,

Istituto CNR[b], Via Tolara di Sotto 89, I-40064 Ozzano, Italia, and

Istituto Chimico „G. Ciamician", Universita di Bologna[c], Via Selmi 2, Bologna, Italia

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A recently proposed direct 1,5-$n_N n_O$ through-space interaction in the azabicyclo-[2.2.2]octanone **1** has been confirmed experimentally by investigating the isomeric tropinone urethane **3**. In **3** the corresponding homoconjugative matrix element $< n_N \mid H \mid n_O >$ vanishes by reasons of topology and local symmetry. The combined application of photoelectron (PE) and electron transmission (ET) spectroscopy allows the distinct differentiation between influences upon symmetric $\pi$ and antisymmetric $\pi^*$ orbitals. It has been found that the urethane group $NCO_2CH_3$ in **4** exerts an inductive effect virtually identical with that of the oxygen atom in **7**. The variable temperature NMR spectra of **3**, **4** and **6** have been interpreted in terms of hindered N–CO rotations and not, as has been claimed in the case of **6**, as O–CO rotation. The CC double bond in dehydrotropinone **4** turns out to increase the rotational barrier, a phenomenon which is explained by the local symmetry and topology of this tropinone skeleton and is further supported by the PES and ETS measurements.

**Intramolekulare Wechselwirkungen und behinderte Rotation in Tropinon-urethanen: Eine kombinierte PE-, ET- und DNMR-spektroskopische Untersuchung[1)]**

Eine kürzlich postulierte 1,5-$n_N n_O$ through-space-Wechselwirkung im Azabicyclo-[2.2.2]octanon **1** wurde mit Hilfe des isomeren Tropinon-urethans **3** experimentell bestätigt. In **3** verschwindet aus topologischen und lokalsymmetrischen Gründen das entsprechende Matrixelement $< n_N \mid H \mid n_O >$. Die kombinierte Anwendung der Photoelektronen- (PES) und Elektronentransmissionsspektroskopie (ETS) läßt die deutliche Unterscheidung zwischen Einflüssen auf symmetrische $\pi$- bzw. antisymmetrische $\pi^*$-Orbitale zu. Es wurde beobachtet, daß die Urethangruppe $NCO_2CH_3$ in **4** einen induktiven Effekt ausübt, der praktisch mit dem des O-Atoms in **7** übereinstimmt. Die temperaturabhängigen NMR-Spektren von **3**, **4** und **6** lassen sich mit behinderter N–CO-Rotation deuten und nicht, wie im Fall von **6** behauptet, mit einer O–CO-Rotation. Es zeigt sich, daß die CC-Doppelbindung in Dehydrotropinon **4** die Rotationsbarriere erhöht, was durch die lokale Symmetrie und Topologie dieses Tropinongerüstes erklärbar ist. Dieser Effekt ist im Einklang mit den Ergebnissen der PES- und ETS-Messungen.


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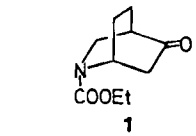
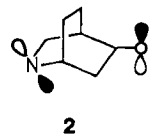
*Peel* and *Holmes*[2] have recently described the PE spectrum of azabicyclo-[2.2.2]octanone **1**. The experimental split of the first two bands (mainly $n_N$ and $n_O$, respectively) of 0.40 eV has been ascribed to the mutually inductive perturbation *as well as* to a remarkable through-space interaction (homoconjugation) between $n_N$ and $n_O$ based on the interpretation by means of HAM/3[3] and Hückel calculations ($\beta_{NO} = -0.19$ eV).




**1**



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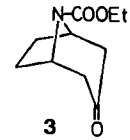


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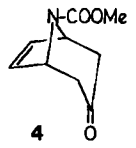


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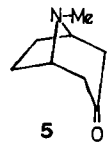


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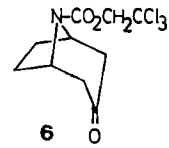


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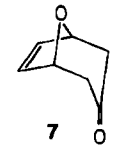



**7**

This interaction is notable as it represents a rarely encountered true 1,5-nn through-space interaction[4] (**2**) and therefore, further experimental evidence would be desirable. If this interaction is dominated by a homoconjugative pathway it can be anticipated that a change in the topology of the molecule – with the effect of rendering any interaction between $n_N$ and $n_O$ negligible but retaining exactly the size of the σ frame – would bring about a reduction in the splitting of the first two PE bands. Towards this aim we investigated the isomeric tropinone derivative **3** and the related compounds **4**–**7**. In order to evaluate the extent of

Table 1. Vertical ionization energies $I_i^m$ in eV and empirical assignment (accuracy is ca. ±0.03 eV, values are rounded to the nearest 0 or 5 in the second decimal place) and calculated orbital energies ($\varepsilon_i = -I_i^m$) of **3**, **4**, **5** and **7**. Values in parentheses are uncertain. The same notation for the orbitals as in ref.[2] is used: $n_O$ refers to the carbonyl oxygen lone-pair, $n_{OE}$ to the ether oxygen in **7**, $n'_O$ and $\pi_{OO}$ are localized in the OCO group. The first and second row show the results according to HAM/3[3] and MINDO/3[7] calculations, resp.

| | $I_1^m$ | $I_2^m$ | $I_3^m$ | $I_4^m$ | $I_5^m$ | $-\varepsilon_i$ | | HAM/3<br>MINDO/3 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **3** | (9.10) | 9.35 | (10.30) | 10.65 | | | | | | |
| | $n_N$ | $n_O$ | $n'_O$ | $\pi_{OO}$ | | $n_O$ | $n_N$ | $\pi_{CC}$ | $n'_O$ | $\pi_{OO}$ |
| | | | | | | 9.03 | 9.22 | | 9.53 | 10.52 |
| | | | | | | 9.65 | 9.27 | | 10.24 | 10.97 |
| **4** | 9.45 | | 9.95 | (10.30) | 10.90 | 9.12 | 9.28 | 9.65 | 9.76 | 10.57 |
| | $n_N$, $n_O$ | | $\pi_{CC}$ | $n'_O$ | $\pi_{OO}$ | 9.23 | 9.69 | 9.99 | 10.70 | 11.06 |
| **5** | 8.55 | 9.15 | 11.25 | | | 9.09 | 8.84 | | 11.29 | ($CH_2$) |
| | $n_N$ | $n_O$ | σ | | | 9.51 | 8.92 | | 10.55 | ($CH_2$) |
| **7** | 9.50 | 9.80 | 10.35 | | | 9.43 | | 9.80 | 10.83 | ($n_{OE}$) |
| | $n_O$ | π | $n_{OE}$ | | | 9.63 | | 9.57 | 10.63 | ($n_{OE}$) |
| **1**[2] | 8.89 | 9.29 | 10.12 | 10.65 | 11.40 | 9.18 | 8.90 | | 10.04 | 10.74 |

the inductive perturbation exerted by the urethane and carbonyl moieties and to ascertain that no through-bond interaction ($n_N$-$\pi^*_{CO}$) falsifies the position of the lone-pair PE bands we applied electron transmission (ET) spectroscopic measurements to **3**–**5**[5,6]. Some consequences for the N–CO rotational barriers are then described.

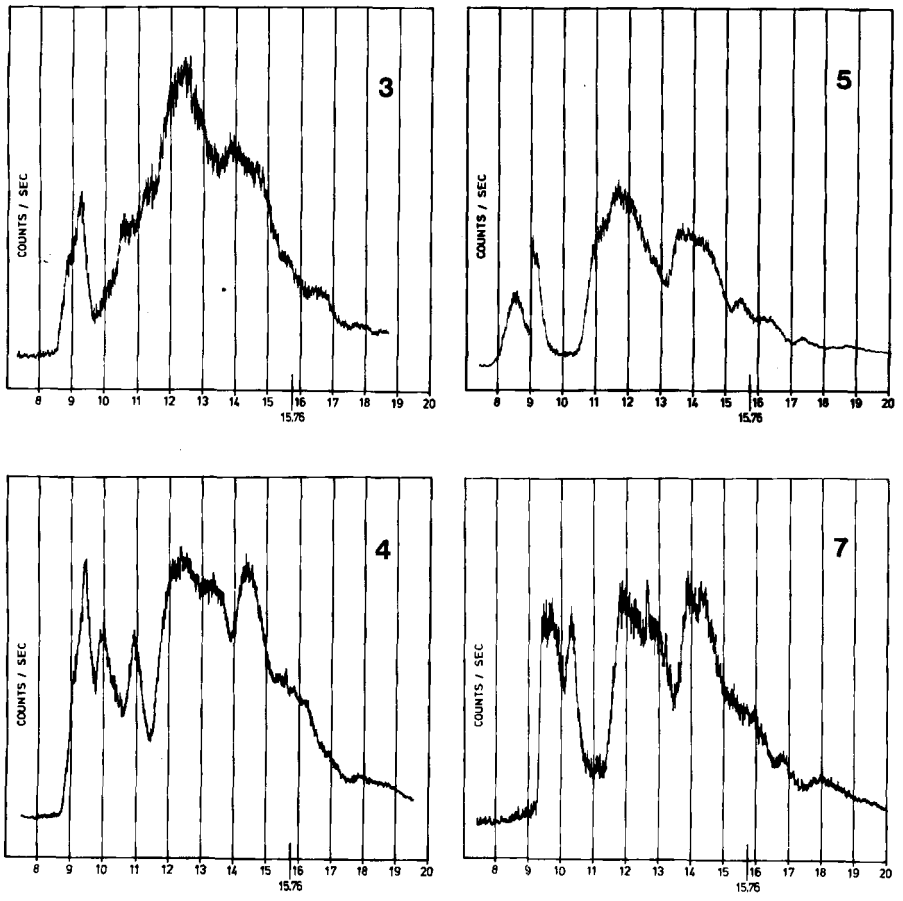



Fig. 1. He(I) Photoelectron spectra of **3**, **4**, **5** and **7**

MM2 calculations[8] have been used to optimize the geometry of **5** and **7**. The values of **5** in Tab. 1 are calculated for an equatorial methyl group. The bicyclic frame of **3** and **4** has been optimized by MM2 as well, the alkoxycarbonyl group was then attached with varying angles of pyramidalization (160–200°C). In addition to that the geometry has been optimized with the aid of the MNDO procedure[7b] varying again the degree of bending (cf. the DNMR section). The

ionization energies for these angles differ as little as 0.1 eV. Thus, an angle of 180° has been taken for **3** and **4**.

The electron transmission spectra of **3**–**5**, i.e. the derivative of the transmitted current as a function of electron energy, are displayed in Fig. 2. The corresponding vertical attachment energies correspond to the negative electron affinities, these are listed in Tab. 2 together with assignments given by the HAM/3[3] method.

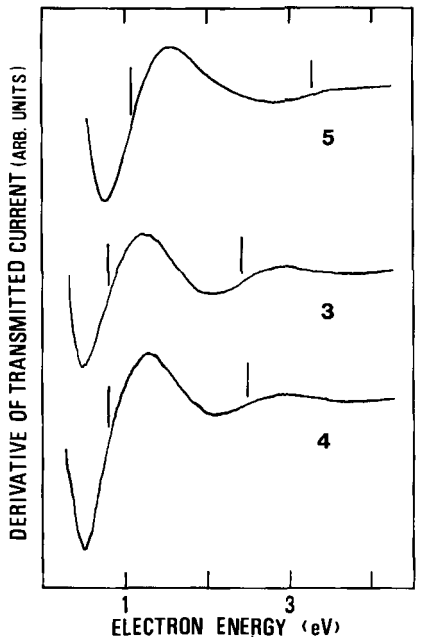



Fig. 2. Derivative of transmitted current as a function of electron energy in **3**, **4** and **5**. The vertical bars locate the vertical electron attachment processes

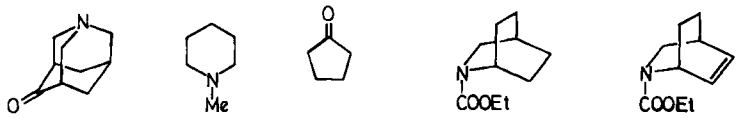
Table 2. Vertical electron affinities in eV (accuracy ± 0.05 eV if two decimal digits are given, ± 0.1 eV if one is given) of **3**, **4** and **5**. Calculated values according to HAM/3. $\pi^*_{CO}$: ring carbonyl LUMO, $\pi^*_{ur}$: urethane moiety LUMO, $\pi^*_{CC}$: CC-π-bond LUMO

| | $EA_i$ | | | $EA_i$ (HAM/3) | | |
|---|---|---|---|---|---|---|
| | | | | $\pi^*_{CO}$ | $\pi^*_{CC}$ | $\pi^*_{ur}$ |
| **3** | −0.80 | | −2.40 | 0.40 | | −1.63 |
| **4** | | −0.81 | −2.55 | 0.14 | −0.19 | −1.71 |
| **5** | −1.09 | −3.3 | | −0.14 | −8.74 ($\sigma^*_{CN}$) | |

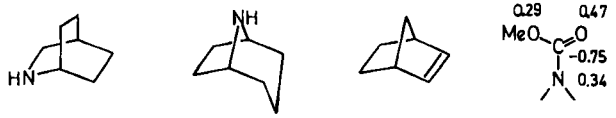
## Discussion

In the following discussion empirical correlations based on known ionization energies of related compounds will be used to confirm or disprove the assignments arrived at by SCF calculations.

Since the $n_O$ orbital of the carbonyl group in tropinone **5** is unable to interact with $n_N$ by reasons of symmetry and the mixing of $n_N$ with $\pi_{CO}$ seems unlikely on account of the considerable energetic separation, the most important influence on $n_N$ will be a polar field effect of the CO group and a possible through-bond interaction with $\pi^*_{CO}$ and $\pi_{CO}$. The former is known to amount to stabilizing 0.27 eV in azaadamantanone **8**[9]. With $I(n_N)$ of **9** as a basis (8.29 eV[10]), a value for tropinone **5** can be predicted, 8.29 + 0.27 = 8.56 eV, which is in excellent accordance with the experiment.




**8** **9** **10** **11** **12**




**13** **14** **15** **16**

At the same time this implies that the influence of $\pi^*_{CO}$ should be negligible. Considering the $\pi^*_{CO}$ electron affinity of **5** ($EA_1$ = −1.09 eV) and comparing this value with the very similar *EA* of unperturbed cyclopentanone (**10**)[11] (*EA* = −1.15 eV) this assumption is immediately corroborated. The remaining second band in the PE spectrum of **5** is then due to ionization from the $n_O$ level.

As regards the interpretation of the urethanes **3** and **4** inspection of the spectra of **1**, **11** and **12** will be very helpful. The carbamate unit, as in **11**[2], displays a characteristic low-energy ionization at 8.43 eV, due to the $n_N$ level, (as to the notation of these orbitals cf. ref.[2]) and a second very much less pronounced ionization event (broad and of low intensity) at 9.67 eV which can be ascribed to the $n'_O$ carbonyl orbital of the carbamate group. The third and usually more intense PE band (in the case of **11** observed at 10.50 eV) belongs to a $\pi_{OO}$ orbital essentially localized on the oxygen atoms of the urethane group.

The most conspicuous feature which attracts attention when comparing the PE spectra of **1**[2] and **3** relates to the split between the first two ionization events $n_N$ and $n_O$, respectively. These two bands overlap strongly in **3** with maxima at ca. 9.10 eV ($n_N$) and 9.35 eV ($n_O$) whereas in **1**[2] distinct maxima at 8.89 and 9.29 eV lead to a considerable split of 0.4 eV. This observation appears to confirm the aforementioned hypothesis. In **1** the homoconjugation between $n_N$ and $n_O$ (cf. **2**) mixes either wave-function to afford linear combinations $n_N - \lambda n_O$ and $n_O + \lambda n_N$, respectively. In **3**, this through-space matrix element $< n_N \mid H \mid n_O >$ vanishes by

reasons of topology and local symmetry and the position of both levels is merely determined by their mutual inductive perturbation and by geometrical factors. It can easily be seen that the stabilization of $n_N$ (**3**) compared with $n_N$ (**1**) is *not* caused by a through-bond orbital interaction with $\pi^*_{CO}$. Compared with cyclopentanone such an interaction would obviously destabilize the $\pi^*_{CO}$ orbital in **5** which is *not* the case. Nor is the stabilization of $n_N$ (**3**) the consequence of an altered inductive field situation in **3** compared with **1**. One may calculate that the inductive field effect contribution is **3** is exactly the same as in **1**. Thus, when applying the following equation[9]

$$\Delta I = \frac{14.39}{\varepsilon}\left(\frac{1}{R_{CN}} - \frac{1}{R_{NO}}\right)\frac{\mu_{CO}}{4.8\,R_{CO}}$$
$$(\varepsilon = 2,\ \mu_{CO} = 2.8\ \text{D},\ R_{CO} = 1.23\ \text{Å})$$

to molecules **1** ($R_{CN}$ = 2.87 Å, $R_{NO}$ = 4.01 Å) and **3** ($R_{CN}$ = 2.84 Å, $R_{NO}$ = 4.05 Å), inductive stabilizations of 0.33 eV (**1**) and 0.35 eV (**3**), resp. result.

There is a further effect which might influence the $n_N$ ionization energy. The bond angle CNC is calculated by MM2 as 112° in **1** but 100° in **3**. Even with a planar situation at the N atom and an unhybridized p-type $n_N$ orbital this geometrical change can affect the $n_N$ ionization energy. The comparison between **13** and **14** shows that this bond angle decrease results in an increase of the $n_N$ ionization energy of ca. 0.25 eV (**13**: $I_{v,1}$ = 8.22 eV[12], **14**: $I_{v,1}$ = 8.5 eV[13]). Therefore we have to consider the possibility that part of the $n_N$ shift is due to this bond angle diminution. On the other hand there can be no doubt that the interaction between $n_N$ and $n_O$ does exist in **1** and vanishes in **3**: HAM/3[3] calculations describe this interaction in **1** by the (normalized) wave function $\phi$ = 0.82 $n_N$ − 0.57 $n_O$ devoid of any through-bond contribution[2] whereas in **3** the mixing coefficient of $n_O$ is zero! Finally we conclude that the lowering of the $\pi^*_{CO}$ level in **3** by ca. 0.3 eV compared with **5** (Tab. 2) can only be explained by the inductive electron-withdrawing effect of the $CO_2C_2H_5$ group (see below) which exerts its influence on the $n_O$ orbital as well: $n_O$ (**3**) is stabilized by ca. 0.2 eV compared with $n_O$ (**5**).

The remaining valence orbitals of the carbamate moiety in **3** are located at similar positions as in urethane **1**. The broad and quite weak ionization beginning at ca. 9.90 eV (maximum at ca. 10.30) can be ascribed to the $n'_O$ level (10.12 eV in **1**) and the maximum at 10.65 eV can be assigned to the $\pi_{OO}$ orbital (10.65 eV in **1**). The difference between the first two electron affinities of **3** $\Delta EA$ = −0.80 + 2.40 = 1.60 eV is satisfactorily reproduced by HAM/3 calculations (Tab. 2) although the absolute values differ somewhat.

In the unsaturated derivative **4** an additional band will be observed in the valence region which is due to the π ionization of the CC double bond. Furthermore the introduction of a π orbital into a saturated system results in a stabilization of other orbitals, particularly of the σ frame. **4** exhibits three distinct ionization processes at 9.45, 9.95 and 10.90 eV. From an inspection of the relative intensities it may be concluded that the first and the second band comprise two ionization events each whereby the first two IE's coincide precisely and the fourth appears as a shoulder on the high-energy flank of the 9.95 eV band. Band 1

corresponds to the inductively stabilized $n_N$ and $n_O$ levels, band 3 has to be ascribed to the similarly stabilized $\pi_{OO}$ orbital and, according to the discussion above, the less intensive shoulder of band 2 originates from the $n'_O$ level. The ionization at 9.95 eV is therefore due to the $\pi_{CC}$ orbital. This energy is by 1 eV higher than the $\pi$ ionization of norbornene (**15**). It is difficult to assess from the PE measurements alone whether this $\pi$ energy stabilization is the consequence of only an inductive perturbation by NCOOR and CO or whether an additional direct homoconjugation between $\pi_{CC}$ and $n_N$ leads to this 9.95 eV position. In this case the results of the ET experiments are most helpful. The $\pi^*_{CC}$ level of **4** appears at 0.81 eV, i.e. accidentally degenerate with the $\pi^*_{CO}$ attachment energy. One may recognize a stabilization compared with norbornene (**15**) (1.70 eV[14]) of 0.9 eV. Since by reasons of local $C_s$ symmetry the $\pi^*_{CC}$ orbital of **4** is unable to interact homoconjugatively with the urethane moiety this stabilization must entirely stem from an inductive perturbation. Thus we may conclude that the high ionization energy of the $\pi_{CC}$ orbital has also to be traced back to inductive effects. On the other hand the $\pi^*_{ur}$ orbital (**16**) to which the nitrogen atom strongly contributes might also be able to interact with $\pi_{CC}$ in a two-electron stabilizing manner. This would entail a raise in the $\pi^*_{ur}$ and a lowering in the $\pi_{CC}$ orbital energy. The latter cannot be assessed because of the lack of a suitable reference compound but the former can be made responsible for the slight increase of the second attachment energy of **4** (2.55 eV (**4**) vs. 2.40 eV (**3**)). A correlation diagram of experimental ionization energies and attachment energies is depicted in Fig. 3.

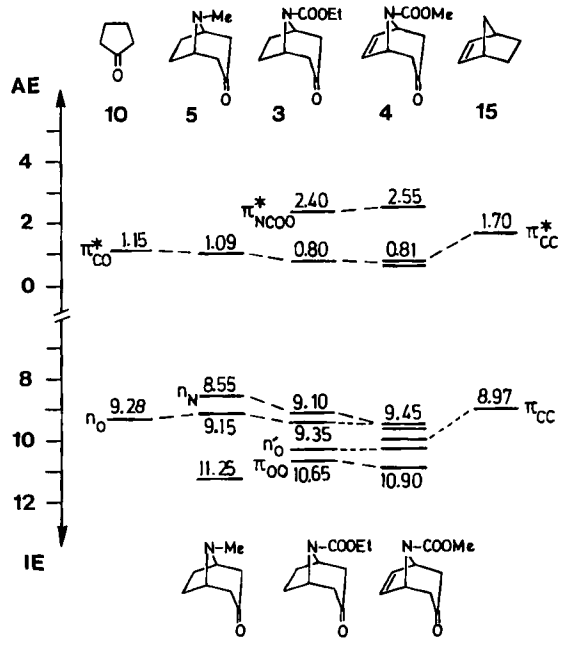
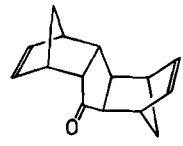



Fig. 3. Ionization and attachment energy correlation diagram for **3**, **4**, **5**, **10**[11] and **15**[14,15]. Energies in eV

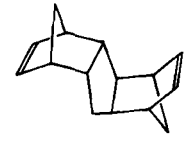
In order to compare the considerable inductive influence of the carbamate moiety with more common atoms or groups we studied the bicyclic ether **7**. A useful starting point for the assignment of the three valence bands at 9.50, 9.80 and 10.35 eV constitutes the oxanorbornene **17**. **17** exhibits ionization events at 9.44 eV ($\pi_{CC}$) and 9.83 eV ($n_{OE}$)[16]. To arrive at reasonable values for **7** it is necessary to modify this spectrum under the influence of an additional γ-keto group.

A good example is given by the *endo-trans-endo* ketone **18**, which shows π ionization energies at 9.31 eV, i.e. 0.37 eV higher than the corresponding diene **19**[17]. Applying this stabilization to the ether **17**, values of 9.44 + 0.37 = 9.81 eV for the π and 9.83 + 0.37 = 10.20 eV for the lone-pair ($n_{OE}$) ionization are obtained, in good agreement with the experimental results. The ionization from the $n_O$ carbonyl lone-pair therefore has to be located at about 9.50 eV, i.e. the first half of the two strongly overlapping PE bands. The HAM/3[3] method satisfactorily reproduces the $n_O$ and π levels but the ether lone-pair orbital is predicted too low. MINDO/3 calculates a wrong sequence.

**17**



**18**



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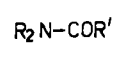

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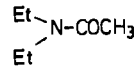

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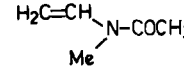

**22**

The comparison of the $\pi_{CC}$ and $n_O$ energies of urethane **4** with those of ether **7** ($\pi_{CC}$: 9.95/9.80 eV, $n_O$: 9.45/9.50 eV) allows the conclusion that the carbamate moiety $NCO_2CH_3$ exerts virtually the same inductive stabilization as the oxygen atom on remote functional groups (in this case CH=CH and C=O). At first sight this seems somewhat surprising when considering the group electronegativity of O and $NCO_2CH_3$, resp. (O: 3.44, $NCO_2CH_3$: 2.62[18]). But within the framework of the principle of electronegativity equalization[18,19] and understanding electronegativity as a tendency to become negatively charged, a qualitatively satisfying answer can be given. The partial charge acquired by an atom or group through chemical combination is proportional to the difference between the final, equalized electronegativity and the initial pre-bonded electronegativity[18]. The equalized electronegativity $X_{eq}$ depends linearly on the charge δ but with a different slope for O and $NCO_2CH_3$ (Fig. 4)[18]. Thus, when combining O and $NCO_2CH_3$ with the same cycloheptenone fragment (group electronegativity 2.40) to form either the urethane **4** or the ether **7**, the resulting equalized electronegativities are very similar ($X_{eq}$ (**4**) = 2.47, $X_{eq}$ (**7**) = 2.44). Since now we are in the region of the intersection of the two straight lines, the gained charge for O and $NCO_2CH_3$ is similar. In

fact, below that value of $X_{eq} = 2.54$ for the intersection, the urethane moiety is predicted to absorb negative charge better than the oxygen atom.

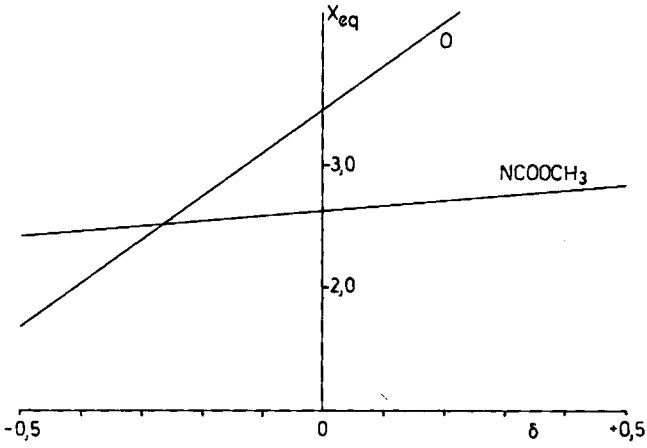


Fig. 4. Variation of equalized electronegativity $X_{eq}$ with charge δ. The straight line has the general expression: $X_{eq} = (X_G/N_G) \cdot \delta + X_G$, where $X_G$ is the group electronegativity and $N_G$ the number of atoms in the group formula[18]. The two straight lines take the form: $X_{eq} = 0.33\ \delta + 2.62$ (**4**) and $X_{eq} = 3.44\ \delta + 3.44$ (**7**). The intersection has the co-ordinates: $X_{eq} = 2.54$, $\delta = -0.26$

## DNMR Studies

Hindered rotation about the N–C bond in carbamates **20** has been the subject of numerous studies[20]. It has been shown that substituent effects in R′ of **20** can satisfactorily be explained by perturbational molecular orbital theory[21]. On the other hand structural modifications within the R groups of **20** have also been studied[22–26]. Conjugations with both *N*-vinyl and *N*-aryl groups result in lower barriers by stabilizing the transition state (conjugation of the nitrogen lone-pair $n_N$ with the unoccupied $\pi^*_{CC}$ level)[24]. The consequences for the urethane pair **3**/**4** should be interesting. By reasons of local symmetry the $n_N$ lone-pair of **4** cannot interact with $\pi^*_{CC}$ in the orthogonal transition state of the N–CO rotation. Thus, no reduced barrier may be predicted as far as the transition state is concerned. If, on the other hand, a significant $\pi_{CC}$-$\pi^*_{ur}$ homoconjugation stabilizes the rotational ground state an enhanced barrier can be anticipated.

A second aspect calls for a determination of rotational barriers in **3**, **4**, and **6**. A recent article[25] claims the observation of a CO–O rotation in *N*-(2,2,2-trichloroethoxycarbonyl)cyanonortropane (and in **6** as well) with an Arrhenius activation energy $E_a = 56.9$ kJ/mol (13.6 kcal/mol), but no $\Delta G^{\neq}$ has been given. However, some doubts may arise regarding the reliability of both this value and its interpretation. First, barriers for CO–O rotations are usually low and $\Delta G^{\neq}$ values are reported to lie between 33 and 42 kJ/mol (8–10 kcal/mol)[20c,27]. Secondly, it is known that $\Delta G^{\neq}$ is much less sensitive to experimental errors than $\Delta H^{\neq}$ or $\Delta S^{\neq}$ [28–31]. Therefore, the value in question for **6** will be $\Delta G^{\neq}$. Thirdly, electron-withdrawing substituents in the R′ part of carbamates tend to raise the

$\Delta G^{\neq}$ barrier for N–CO rotation[21]. According to the PMO model[21] the trichloromethyl group in **6** is therefore predicted to increase the N–CO rotational barrier compared with **3**, and a direct comparison of both $\Delta G^{\neq}$ values would be helpful.

By means of $^{1}H$ and $^{13}C$ dynamic NMR spectroscopy we have studied the hindered rotation around the N–CO bond in the molecules **3**, **4**, and **6**. At low temperatures (265–285 K) the $^{1}H$ spectrum of **6** exhibits a typical AB pattern for the $OCH_2$ protons. This is in contrast to ref.[25] where only two singlets of equal intensity have been reported for **6** and two other similar derivatives in the low temperature range. At higher temperatures (> 314 K) we observe coalescence of the AB spin system to a sharp singlet. The temperature-dependent NMR spectra have then been recorded (Fig. 5), and the first-order rate constant at the coalescence temperature (314 K in [$D_8$]toluene) has been calculated using three methods. First, a complete line shape analysis by means of DNMR 5[32] (Fig. 5) has been performed affording $k = 77\ sec^{-1}$ at $T = 314$ K. Secondly, for the exchange of coupled nuclei in an AB system, the equation $k_c = (\pi/\sqrt{2})\sqrt{(\Delta\nu^2 + 6J^2)}$ has been employed. It has been shown that good results may be obtained for $\Delta\nu > J$[33]. In the case of **6** $\Delta\nu_{AB} \approx 21$ Hz (extrapolated from low temperature measurements in [$D_8$]toluene), $J_{AB}$ equals 12.0 Hz. The application of the equation yields $k_c = 81\ sec^{-1}$ at $T_c = 314$ K. Thirdly, a method has been employed which avoids the use of $\Delta\nu_{AB}$ as experimental parameter[34]. $k_c$ is determined by a single parameter, the width at half height ($W_{1/2}$) of the spectrum at the coalescence point. With $W_{1/2} = 12$ Hz a value of $k_c \approx 75\ sec^{-1}$ is calculated using the $J = 12$ Hz curve in ref.[34]. In Table 3 the results of these three methods are given.

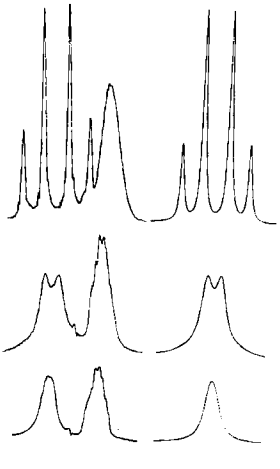

Fig. 5. Temperature dependence of the $^{1}H$ NMR spectrum of **6** in [$D_8$]toluene. The depicted spectral range comprises the $OCH_2$ and bridgehead protons. Temperatures (from below): 315, 308, 275 K

Calculated error limits are standard deviations and are composed of errors in temperature $\Delta T = \pm 2$ K (actual accuracy is thought to be better) and in the rate constant $\Delta k \approx \pm 15\%$ due to estimated $d\Delta\nu$, $d\Delta W$ (experimental band width variations) and imperfect bandfitting.

It can be seen that all three methods arrive at the same rate constants $k_c$ and $\Delta G^{\neq}$ within the error limits.

Table 3*). Dynamic NMR data

| Comp. | $T_c$/K | $\Delta\nu_c$/Hz | $k_c$/sec$^{-1}$ | $\Delta G^{\neq}$/kJ/mol (kcal/mol) |
|---|---|---|---|---|
| **6**[a] | 314 | 21 | 77 | 65.6 ± 0.8 (15.7 ± 0.2) |
| **6**[b] | 314 | 21 | 81 | 65.5 (15.6) |
| **6**[c] | 314 | $W_{1/2}$ = 12 | 75 | 65.7 (15.7) |
| **6**[d] | 309 | 25 (C-6, 7) | 55 | 65.4 (15.6) |
| **6**[d] | 301 | 14 (C-2, 4) | 31 | 65.1 (15.6) |
| **3**[d] | 286 | 21.4 (C-6, 7) | 47 | 60.7 (14.5) |
| **3**[e] | 295 | 41.0 (C-6, 7) | | 61.2 (14.6) |
| **3**[d] | 280 | 13.4 (C-2, 4) | 30 | 60.5 (14.5) |
| **3**[e] | 287 | 24.9 (C-2, 4) | | 60.6 (14.5) |
| **4**[d] | 292 | 13.5 (C-2, 4) | 30 | 63.2 (15.1) |

*) $\Delta G^{\neq}$ has been calculated according to $\Delta G^{\neq} = 4.575 \cdot 10^{-3} \cdot T\,[10.319 + \log(T/K)]$ (kcal/mol).

[a] Complete line shape analysis. – [b] $k_c = (\pi/\sqrt{2})\sqrt{(\Delta\nu^2 + 6J^2)}$. – [c] using method in ref.[34]. – [d] $k_c = \pi\Delta\nu/\sqrt{2}$, $^{13}$C NMR. – [e] ref.[23]. $J_{AB}$ = 12.0 Hz.

The $^{13}$C NMR spectrum of **6** shows exchange broadening at ambient temperature. Below 0°C this dynamic process is frozen and the symmetry of the molecule lost. The resonances of the pairs C-6/C-7, C-2/C-4 and C-1/C-5 are now split, $\Delta\nu$ becomes 0.91, 0.55, and 0.09 ppm, resp., at −16°C. According to these different splittings three coalescence temperatures have been observed: ≈ 10°C (C-1/C-5), 28°C (C-2/C-4), and 36°C (C-6/C-7). Only the two latter have been used for the determination of $\Delta G^{\neq}$. As can be seen from the data of Table 3 the agreement with the results of the $^1$H measurements is excellent. The urethane **3** has been reported[25] to display no splitting for the $OCH_2$ protons at lower temperatures. We confirm this observation, but find an exchange broadening in the range of 2–3 ppm. The diastereotopic $OCH_2$ protons are either fortuitously isochronous even in a conformationally frozen state or the corresponding barrier is much lower than in the case of **6**. The latter possibility, however, seems very unlikely in view of the observed exchange phenomena at about 2–3 ppm. It was therefore decided to investigate the $^{13}$C dynamic behaviour. The inspection of the room temperature spectrum of **3** already reveals a similar broadening as in **6**. At −33°C the splittings

of the respective signals become 0.84 (C-6/C-7), 0.53 (C-2/C-4), and 0.11 ppm (C-1/C-5). It can be seen that the $\Delta\nu$ values are nearly independent of the nature of alkoxy group when compared with **6**. The influence upon the rotational barrier, however, is significant as can be seen from the data in Tab. 3.

Finally urethane **4** was measured in order to obtain some insight into the abovementioned effect of a σ-symmetrical π-bond. Tab. 3 shows that the barrier for **4** is slightly raised but at all events *not* lowered.

We are now in a position to give some explanations for these phenomena. First, the conformational processes in **3**, **4**, and **6** cannot be traced back to O–CO rotations, since neither the barrier heights nor the low-temperature AB spin system of **6** are compatible with such a suggestion. On the other hand, N–CO rotations are in full agreement with the experimental observations from both the energetic[23,35] and topological aspect. Secondly, the higher barrier (by 1.1 kcal/mol) in the trichloro derivative **6** compared with **3** reflects the lower availability of the $CCl_3CH_2O$-oxygen lone-pair. Therefore, the transition state[21b], is *less* stabilized than in the case of **3**, and the ground state[21a] is *more* stabilized by inductive lowering of $\pi^*_{CO}$. Thirdly, the slight but nevertheless significant increase in the barrier height going from **3** to **4** confirms our expectations. The double bond is obviously incapable (primarily by reasons of symmetry) of stabilizing the $n_N$ lone-pair in the orthogonal transition state but may render the ground state more stable by a two-electron $\pi_{CC}$-$\pi^*_{ur}$ interaction. With reservation we may therefore conclude that the slight raise of the $\pi^*_{ur}$ orbital energy (as discussed above) is due to this 1,3-homoconjugation. Some justification for such an effect may be also obtained by considering the calculated bond angles C-1/N/C-5 in **3** and **4**. Introduction of the double bond diminishes the C-1/N/C-5 angle by about 2.5°. This should decrease the rotational barrier in contrast to the experimental finding.

It is not known whether the rotating ester group holds a planar or pyramidalized position. Inversion barriers of tropinone urethanes are predicted to be rather low taking into account the published data of a series of cyclic amines[36] including tropanes[37]. In three-membered rings, like triaziridines[38], the nitrogen of the carbamate group is strongly pyramidalized, but in larger rings and acyclic urethanes it seems to prefer a planar conformation[39]. This is also borne out by MNDO and MINDO/3 calculations carried out for urethane **4** allowing for full geometry

Table 4. Dependence of SCF energy on the angle $\Theta$ (degree of pyramidalization, see text) for urethane **4**

| $\Theta$ | $\Delta H_f^\circ$ (kcal/mol) MNDO | MINDO/3 |
|---|---|---|
| 163.5° | −83.67 | |
| 180° | −83.22 | |
| 205° | −83.52 | |
| 177.8° | | −91.95 |
| 180.8° | | −91.96 |
| 181.9° | | −91.95 |

optimization at various degrees of pyramidalization. If an angle $\Theta$ is defined between the N–CO bond and the line bisecting the C-1/N/C-5 angle, the calculated dependence of total energy on $\Theta$ will convey some impression of the ease with which this bending may take place. The data in Table 4 show that this potential curve possesses a very broad flat minimum. The assumption of an almost planar situation at the nitrogen atom is therefore supported by these SCF models.

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## Experimental Part

The variable temperature $^1$H NMR spectra were recorded on a Bruker WP-80 spectrometer in continuous wave mode. All variable temperature $^{13}$C NMR spectra have been measured on solutions in $CDCl_3$ using a Varian XL-100 spectrometer. The temperatures were determined by a thermocouple placed inside a sample tube containing the respective solvent. PE spectra: Leybold-Heraeus UPG 200, calibration against Ar and Xe. ET spectra: Vertical attachment energies, i.e. the negative of the electron affinities, were determined by means of an electron transmission spectrometry (ETS) apparatus in the format devised by *Sanche* and *Schulz*[5] and described in ref.[40]. The sharp variations in the resonance scattering cross section, as a function of the impact energy, are enhanced by recording the first derivative with respect to energy of the electron beam current transmitted through the gas cell. The present data were obtained setting the retarding voltage of the analyzer as close as possible to that of the filament, so that they are correlated with the nearly total scattering cross section[41]. The reported attachment energies correspond to the vertical midpoints between the minima and the maxima of the derivatized signal. The energy scales were calibrated to within $\pm$ 0.05 or $\pm$ 0.1 eV, depending on the number of decimal digits reported, by reference to the $(1\,s^1\,2\,s^2)^2S$ anion state of He.

Compounds **3** and **5** are commercially available (Janssen Chimica). **4**, **6** and **7** have been prepared according to ref.[42].

CAS Registry Numbers

**3**: 32499-64-2 / **4**: 53416-89-0 / **5**: 532-24-1 / **6**: 53912-86-0 / **7**: 40458-77-3

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