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A LOW ENERGY BARRIER FOR ROTATION AROUND CARBON-CARBON DOUBLE BOND

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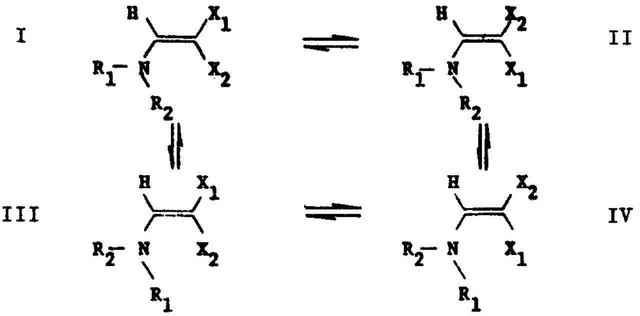
Isomerization around a double bond may be regarded as a torsional process involving rotation around the sigma bond axis of this system (2,3). Activation energies for thermal isomerization of olefins are 25-65 kcal/mol (2). Extensive delocalization of the π electrons of the double bond, in the ground state of the molecule, is expected to lower the activation energy for this process (3). A simple resonance picture provides one way of qualitatively describing such a situation. Considering the formal structure I, its electrons distribution may be represented qualitatively by Ia. The groups X_1 and X_2 are capable of stabilizing a negative charge, while the nitrogen atom, on the second trigonal carbon, bears a positive charge. The structure of Ia clearly implies reduction of the bond order of the formally localized double bond in I and a concomitant increase of the orders of the C-N and C-X bonds. Activation energy for a torsional process around a covalent bond depends, among other factors, on the π electron density associated with this bond (3).

I

I_a

It is of interest to investigate whether the energy barrier for rotation around a carbon-carbon double bond can be sufficiently reduced to allow the establishment of a dynamic equilibrium between the rotamers I and II (Fig. 1) in the ground state of the system. The complete equilibrium must also include the transformation I$\rightleftharpoons$III and II$\rightleftharpoons$IV, which are associated with restricted rotation around the C-N bond (4).

FIG. 1

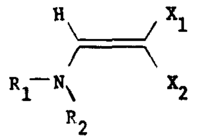


A third type of equilibrium, which may exist, involves the inversion of the pyrimidal nitrogen atom. On the time scale of our measurement (nmr) this process would be fast (5), and therefore for symmetry analysis the nitrogen atom may be considered planar. For the sake of simplifying the equilibrium system in Fig. 1, we have first investigated the compounds where $X_1=X_2$ and $R_1=R_2$. For such a case, the two types of equilibria, I$\rightleftharpoons$II and I$\rightleftharpoons$III, involve equivalent structures. In any of the equivalent conformers, the two constitutionally equivalent X groups are diastereomerically related (6) in the min energy (E_{min}) conformation of the molecule (vida infra). They should, therefore, in principle, exhibit two chemically shifted signals in the nmr spectrum. Similar analysis applies to the two R groups.

The olefins listed in Table 1 have been prepared from the corresponding methoxy or ethoxymethylene compounds by reaction with the appropriate secondary amine (7). Their gross structure has been confirmed by comparison of physical properties to literature data, by elementary analysis, and by nmr and mass spectra.

The most striking feature in the nmr spectra of these compounds (Table 1) is the reversible temperature dependence of the shape of the X signals, and also of the R signals. The general behavior clearly indicates that the two X groups and also the two R groups, are involved in a kinetic process whereby they exchange their identities (8). The free energy of activation for the observed process at the temperature of coalescence (t_c) was calculated in the usual way (8) from the max chemical shift separation of the two equal intensity signals ($\Delta\delta$) and from t_c using Eyring equation (transmission coefficient was taken as unity). All experimental data points towards rotation around the C-C double bond as the process responsible for the interchange of the two X groups, which was observed in the nmr spectra. Plausible different interpretations do not fit the experimental results. Conformational exchanges which might be associated either with rotation around the C-X bond or the-O-R bond (in the di-esters series) are incompatible with observed nmr spectra. The conceivable addition-elimination of an amine (possibly present as an impurity) to the double bond, which could provide a route for the interconversion I$\rightleftharpoons$II, has been ruled out. Thus, the addition of dimethyl amine to a solution of 2 in CH_2Cl_2 did not cause a detectable change in the rate of coalescence of either

TABLE I. N.M.R. Data.[a]



Compd.	R_1	R_2	X_1	X_2	$X_1;X_2$			$R_1;R_2$			Solvent[b]
					$\Delta\delta$[e] cps	tc °C	$\Delta G^{\ddagger}$ kcal/mol	$\Delta\delta$[e] cps	tc °C	$\Delta G^{\ddagger}$ kcal/mol	
1.	CH_3	CH_3	$CO_2C_2H_5$	$CO_2C_2H_5$	3.4[c]	22.0	16.0	21.7	-13.5	13.0	CH_2Cl_2
2.	CH_3	CH_3	CO_2CH_3	CO_2CH_3	5.0	18.5	15.6	22.8	- 9.0	13.3	CH_2Cl_2
3.	CH_3	p-methoxy phenyl	CO_2CH_3	CO_2CH_3	8.2	76.5	18.5				$CHBr_3$
4.	CH_3	phenyl	CO_2CH_3	CO_2CH_3	7.2	90.0	19.4				$CHBr_3$
5.	CH_3	p-nitro phenyl	CO_2CH_3	CO_2CH_3	5.5	137.	22.1				$CHBr_3$
6.	CH_3	CH_3	$COCH_3$	$COCH_3$		<-40	<12[d]	33.9	-11.0	12.9	CH_2Cl_2
7.	CH_3	p-methoxy phenyl	$COCH_3$	$COCH_3$	∿5[f]	∿-30	<13[g]				CH_2Cl_2
8.	CH_3	phenyl	$COCH_3$	$COCH_3$	6.2	-6.5	13.9				CH_2Cl_2
9.	CH_3	p-nitro phenyl	$COCH_3$	$COCH_3$	4.8	42.5	16.9				CH_2Cl_2

[a] Nmr spectra were recorded on Varian HA-60 spectrometer, equipped with variable temperature probe and thermo-regulating unit. The temperature is accurate to ±1°C. [b] 7-12% solute concentrations were used. [c] measured for the methyl signals. [d] No peak separation could be attained down to -40°C, but broadening was noticed. The upper limit of $\Delta G^{\ddagger}$ was estimated using t_c = -40°C and $\Delta\delta$ = 5.4 cps. [e] Max chemical shift separation determined at low temperature. [f] Two broad signals of unequal intensity were observed. [g] Estimated value using t_c = 30°C, $\Delta\delta$ = 5 cps and neglecting unequal population.

the methoxyls or the dimethylamino signals. It is noteworthy that in the nmr spectra of the methoxymethylene compounds, which are the precursors of the corresponding aminomethylene compounds, the two X groups give rise to two chemically shifted signals which do not respond to temperature variations.

Nmr results require that in the E_{min} conformations of the two interchanging species (I and II), the two X groups should be diastereomerically related (6). This can be realized either in an all planar structure, or if steric interactions prevail, in a twisted conformation where the X-C-X plane makes an angle of any value, except 90°, with the C=C-H plane. The 90° twisted form (X groups are enantiomerically related (6)) is probably the max energy conformation required for the interchange of the two X groups. Similar symmetry analysis can be invoked to describe the conformations associated with the two interchanging R groups, as it has been observed in the nmr.

Should our interpretation be correct, then certain qualitative correlations between $\Delta G^{\ddagger}$ values, for the two rotational processes, and the electronic nature of the double bond substituents should be predictable. By resonance argument, enhancement of the capacity of the X groups to stabilize a negative charge should decrease $\Delta G^{\ddagger}$ for rotation around C=C bond and increase $\Delta G^{\ddagger}$ for rotation around C-N bond. An inversed trend is predicted for R groups which are capable of interacting competitively with the nitrogen lone pair. Accordingly, $\Delta G^{\ddagger}$ of 6 is lower than those of the di-esters 1 and 2 for C=C rotation. The $\Delta G^{\ddagger}$ value of 6 (C-N rotation) might be expected to be higher than those of 1 and 2, but all three values have been found to be similar (9). Replacement of one N-methyl by a phenyl group in both 2 and 6 (to give 4 and 8 respectively) is accompanied, as predicted, by an increase in $\Delta G^{\ddagger}$ (C=C rotation) of 3.8 and 1.9 kcal/mole respectively. Furthermore, the above predicted trends have been confirmed by the introduction of p-methoxyl and p-nitro functions into the N-phenyl group of 4 and 8. Thus, while the p-methoxyl substitution (3 and 7 respectively) is accompanied by a decrease in the $\Delta G^{\ddagger}$ values (C=C rotation), the p-nitro substitution (5 and 9 respectively) results in a substantial increase in the $\Delta G^{\ddagger}$ (C=C rotation).

The equilibrium $I \rightleftharpoons III$ (Fig. 1) must also be considered wherever $R_1 \neq R_2$. In the range of temperatures where nmr exchange effects have been observed for C=C rotation, no such effects could be detected with respect to C-N rotation, except for 7 (of course, this does not exclude the existence of the equilibrium $I \rightleftharpoons III$). Indeed, in this series ($R_1 \neq R_2$), the nitrogen lone pair in 7 is the least delocalized by the aromatic N-substituent and the most delocalized by the two X groups. This accounts for the observation that in 7 the diacetyl singlet splits upon cooling into two unequal intensity broad signals with concomitant broadening of the N-methyl signal (10) (∿4 cps at -35°).

In conclusion, our experimental results support the dynamic model for the delocalized systems where two kinds of torsional processes have been detected. One could not a priori exclude a synchronus mode of rotation of the two systems, involving the p orbital of the nitrogen atom and one p_{π} orbital of the double bond. Inasmuch as different $\Delta G^{\ddagger}$values have been found for the two rotational processes this, most probably, is not the case. Further work is under way to clarify this point and various other aspects of this phenomenon.

REFERENCES

1. Present address: Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Israel.
2. S. W. Benson, The Foundation of Chemical Kinetics, McGraw-Hill Book Co., Inc., (1960) pp. 254-256.
3. M. Calvin and R.E. Buckles, J.Am.Chem.Soc., 62, 3324 (1960)
4. H.E. Kramer and R. Gomper, Z.Physik.Chem., 43, 292, 349 (1964);A. Mannschreck and U. Koelle, Tetrahedron Letters, 863 (1967).
5. D.L. Griffith and J.D. Roberts, J.Am.Chem.Soc., 87, 4089 (1965), and references cited there.
6. K. Mislow, Introduction to Stereochemistry, W.A. Benjamin Inc., New York, (1965), pp. 72-73.
7. F. Claisen, Cenn., 297, 5, 78 (1897)
8. H.S. Gutowsky and C.H. Holm, J.Chem.Phys., 25, 1228 (1956); A. Allerhand, H.S. Gutowsky, J. Jonas and R.A. Meiner, J.Chem.Soc., 88, 3185 (1966).
9. We shall comment on this apparent discrepancy in the full account.
10. The lack of any nmr exchange effects associated with C-N rotation when $R_1 \neq R_2$ on one hand and, on the other hand, its observation in the spectrum of 7, imply that the life time of conformations involved in this process is short on nmr time scale. Actually, it is irrelevant to our argument of qualitative correlation of $\Delta G^\ddagger$ with the electronic nature of the substituents, whether we are measuring the equilibrium I $\rightleftharpoons$ II or III $\rightleftharpoons$ IV or rate contributions from both of them.