

The Stevens Rearrangement : an Antiaromatic Pericyclic Reaction ?

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The possibility that the Woodward–Hoffmann rules may break down quite generally for very exothermic reactions is discussed. MINDO/3 Calculations for a pericyclic mechanism for the Stevens rearrangement support this possibility. Although a concerted mechanism for the Stevens rearrangement is formally 'forbidden' according to the Woodward–Hoffmann rules, the calculated activation energy is extremely small (17 kJ mol^{-1}). The calculated structure of a benzoyl-stabilized nitrogen ylide is reported and the electrostatic energy of the ylide is estimated.

In the classic article by Woodward and Hoffmann¹ on pericyclic reactions, the section headed 'Violations' begins with the sentence 'There are none!'. Woodward and Hoffmann suggest that reactions in which orbital symmetry is not conserved cannot take place *via* a concerted pericyclic mechanism and they explain several apparent examples of 'forbidden' reactions in

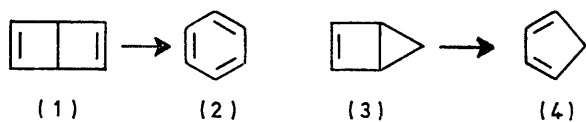
¹ R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

terms of alternative mechanisms involving biradical intermediates.

In an alternative theory of pericyclic reactions which was first proposed by Evans,² the facility of the reactions depends on the resonance stabilization of the

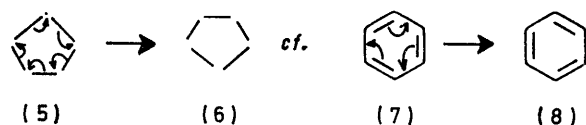
² (a) M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, 1938, **34**, 614; (b) M. G. Evans, *ibid.*, 1939, **35**, 824; (c) M. J. S. Dewar, *Chem. Soc. Special Publ.*, No. 21, The Chemical Society, London, 1967; (d) *Angew. Chem. Internat. Edn.*, 1971, **10**, 761.

corresponding transition states. Reactions which follow the Woodward–Hoffmann rules have transition states which are aromatic while reactions which violate the rules have antiaromatic transition states. Reactions of the latter kind should have correspondingly high activation energies and so occur correspondingly less readily; nevertheless they should be feasible and should indeed occur in cases where no better alternatives exist. This seems to be so in the ‘forbidden’ electrocyclic conversion of Dewar benzene (1) into benzene (2) and of the bicyclopentene (3) into cyclopentadiene (4). In each case rearrangement *via* an intermediate biradical is ruled out by steric considerations and MINDO/3 calculations strongly suggest that both these reactions [(1) \rightarrow (2) and (3) \rightarrow (4)] do indeed involve concerted antiaromatic pericyclic processes.³



The purpose of this paper is to point out an alternative way in which the effects of antiaromaticity may be evaded, thus leading to the possibility of true pericyclic reactions violating the Woodward–Hoffmann rules.

A pericyclic reaction involves a cyclic permutation of bonds around a ring of atoms, the process being analogous to the conversion of one Kekulé structure for a cyclic polyene into the other, *i.e.*:

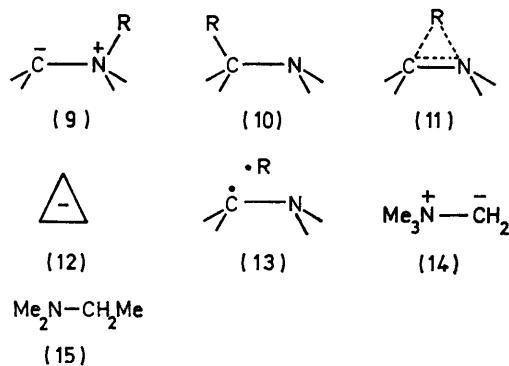


The intermediate phases of such a reaction can thus be represented by superpositions or hybrids of the initial and final structures. The resulting resonance energy will then be positive or negative, depending on whether the system in question is aromatic or antiaromatic, and the magnitude of this resonance energy will be greater, the more evenly the structures are mixed. The effects of aromaticity or antiaromaticity will therefore be greatest at a point midway between reactant and product.

Now according to the Bell–Evans–Polanyi (BEP) Principle,^{4–6} the more exothermic a reaction, the lower in general will be its activation energy and the nearer the transition state will be to the reactants in structure. In the case of a very exothermic pericyclic reaction, the effects of aromaticity and antiaromaticity on the

transition state should then be small because it will have only a small contribution from the product structure. The distinction between aromatic and antiaromatic pericyclic reactions should therefore diminish as the reactions become increasingly exothermic. Since, moreover, a very exothermic reaction should, according to the BEP principle, have a correspondingly low activation energy, one might expect very exothermic antiaromatic pericyclic reactions to occur quite readily. This then would represent an area where the Woodward–Hoffmann rules might break down quite generally.

An interesting possible example of this kind is provided by the Stevens rearrangement of nitrogen ylides (9) to tertiary amines (10).⁷ This reaction violates the Woodward–Hoffmann rules and if it were concerted, the corresponding pericyclic transition state (11) would be isoconjugate with the cyclopropenyl anion (12) and so be antiaromatic. The reaction should also be very exothermic because it involves a large decrease in charge separation and a corresponding large decrease



in coulombic energy. Moreover, a reasonable alternative non-concerted reaction path is available, by fission to a pair of radicals (13) which can recombine to (11), and a number of experimental studies have been recently reported in which attempts were made to distinguish between these two mechanisms.

Until recently no theoretical procedures were available that could give meaningful predictions for such a reaction. *Ab initio* SCF MO methods, apart from doubts concerning their accuracy, would be far too expensive while all the available semiempirical methods would have been suspect due to their tendency to overestimate the stabilities of small rings. Recently, however, an improved version (MINDO/3)⁸ of the MINDO semiempirical SCF MO method has been developed in these laboratories which seems to avoid the systematic errors inherent in MINDO/2⁹ and MINDO/2'.¹⁰ Here we report its application to the simplest known Stevens rearrangement, that of trimethylammonium methylide (14) to dimethylethylamine (15). In view of the current

⁸ R. C. Bingham, M. J. S. Dewar, and D. H. Lo, unpublished work.

⁹ (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 590; (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, p. 3854.

¹⁰ N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1972, **94**, 5303.

³ M. J. S. Dewar and S. Kirschner, unpublished work.

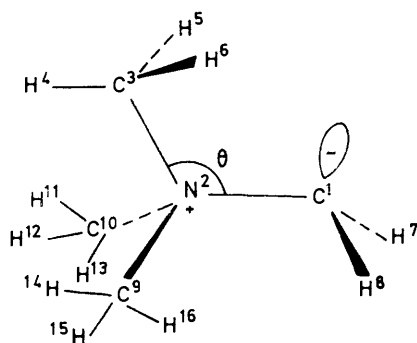
⁴ See M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969.

⁵ G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

⁶ M. J. S. Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 261.

⁷ (a) T. S. Stevens, *Progr. Org. Chem.*, 1968, **7**, 48; (b) A. R. Lepley and A. G. Giumanini, 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley, New York, 1971, vol. 3, p. 297.

interest in ylides, we have also carried out calculations for a benzoyl derivative of (14).



Reaction co-ordinate: θ

Symmetry conditions during optimization

$$\overline{17} = \overline{18}$$

$$\overline{29} = \overline{210}$$

$$\overline{1011} = \overline{1012} = \overline{1013} = \overline{914} = \overline{915} = \overline{916}$$

$$\overline{218} = \overline{217}$$

$$\overline{921} = \overline{1021}$$

$$\overline{11102} = \overline{12102} = \overline{13102} = \overline{1492} = \overline{1592} = \overline{1692}$$

FIGURE 1 Reaction co-ordinate and symmetry conditions for the Stevens rearrangement of trimethylammonium methylide to ethyldimethylamine

Theoretical Procedure.—The calculations were carried out by the MINDO/3 procedure,⁸ details of which are

the same value for an atom in a molecule as for the corresponding free atom but rather is treated as a parameter and different values are used for 2s and 2p AO's. The Z 's appear only in the calculations of overlap integrals, used in the Mulliken approximation for the one-electron core resonance integrals.

The geometries were calculated in all cases by minimizing the total energy, using the SIMPLEX method. In order to reduce the amount of computation in the case of (14), symmetry conditions were assumed as indicated in Figure 1. The conversion of (14) into (15) was studied by using the $\text{H}_3\text{C}-\text{N}-\text{CH}_2$ angle θ (see Figure 1) as reaction co-ordinate. For each value of θ , the energy was minimized with respect to all the other co-ordinates, subject to the assumed symmetry conditions.

RESULTS

The calculated geometries and heats of formation of (14) and (15) are shown in Figures 2a and b. The reaction is predicted to be very exothermic (ΔH -363 kJ mol⁻¹). Figure 3 shows a plot of the energy as a function of the reaction co-ordinate θ (see Figure 1). This should correspond to the concerted conversion of (14) into (15) since the single determinant description used in MINDO/3 greatly overestimates bond dissociation energies and so cannot be

Structure	Bond length (Å)	Bond angles (°)	Dihedral angles (°) *
 (a) Trimethylammonium methylide	$\overline{12} = 1.471$; $\overline{23} = 1.479$ $\overline{34} = 1.118$; $\overline{35} = 1.116$ $\overline{36} = 1.115$; $\overline{17} = \overline{18} = 1.133$ $\overline{29} = \overline{210} = 1.499$ ΔH_f , 415.0 kJ mol ⁻¹	$\overline{123} = 105.1$ $\overline{234} = 114.2$ $\overline{235} = 113.1$ $\overline{236} = 113.1$ $\overline{217} = \overline{218} = 109.8$ $\overline{129} = \overline{1210} = 113.8$	$\overline{1234} = 179.0$ $\overline{1235} = 59.1$ $\overline{1236} = 298.9$ $\overline{3218} = \overline{7123} = 126.5$ $\overline{3129} = \overline{10213} = 119.0$
 (b) Dimethylethylamine	$\overline{12} = 1.435$; $\overline{13} = 1.499$ $\overline{34} = 1.112$; $\overline{35} = 1.112$ $\overline{36} = 1.112$; $\overline{17} = \overline{18} = 1.130$ $\overline{29} = \overline{210} = 1.415$ ΔH_f , 52.2 kJ mol ⁻¹	$\overline{213} = 118.8$ $\overline{134} = 117.0$ $\overline{135} = 112.6$ $\overline{136} = 112.6$ $\overline{217} = \overline{218} = 109.8$ $\overline{129} = \overline{1210} = 119.6$	
 (c) Transition state	$\overline{12} = 1.452$; $\overline{23} = 1.503$ $\overline{34} = 1.138$; $\overline{35} = 1.119$ $\overline{36} = 1.119$; $\overline{17} = \overline{18} = 1.128$ $\overline{29} = \overline{210} = 1.489$	$\overline{123} = 80.0$ $\overline{234} = 105.2$ $\overline{235} = 119.0$ $\overline{236} = 119.7$ $\overline{217} = \overline{218} = 114.1$ $\overline{129} = \overline{1210} = 117.1$	$\overline{1234} = 178.9$ $\overline{1235} = 67.4$ $\overline{1236} = 290.3$ $\overline{3218} = \overline{7123} = 122.5$ $\overline{3129} = \overline{10213} = 115.4$

* Dihedral angle \overline{ijkl} is defined as the angular displacement of the \overline{kl} distance relative to the \overline{ij} one measured anticlockwise along the direction $j \rightarrow k$.

FIGURE 2 Calculated geometries (a) of (14); (b) of (15); and (c) of the pericyclic transition state for conversion of (14) into (15).

being published elsewhere. This differs from the original version of MINDO/2⁹ only in two respects. First, the one-centre integrals are estimated by a modification of Oleari's method;¹¹ secondly, the effective nuclear charge (Z) is no longer assumed to have

used to follow such processes [*e.g.* (14) \rightarrow $\text{Me}_2\text{NCH}_2\cdot + \text{C}\cdot\text{H}_3$]. The reaction was followed in both directions, the

¹¹ (a) L. Oleari, L. Di Sipio, and G. De Michelis, *Mol. Phys.*, 1966, **10**, 97; (b) M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, 1972, **94**, 5296.

forward and backward paths being identical. This suggests that θ is a satisfactory reaction co-ordinate.¹² The conversion of (14) into (15) is predicted to have a very low activation energy (17 kJ mol⁻¹); the structure of the transition state is shown in Figure 2c.

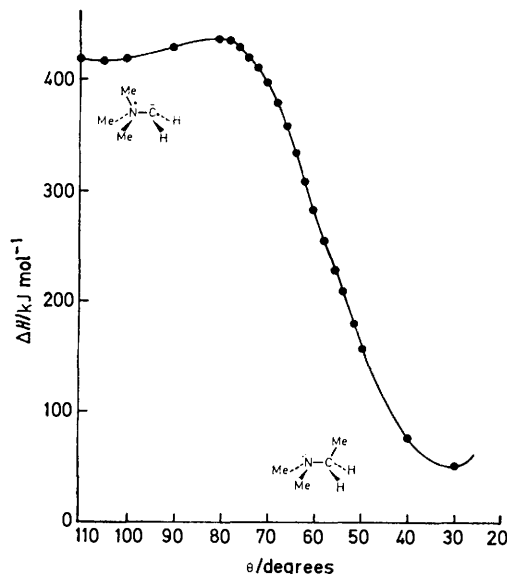


FIGURE 3 Plot of the calculated heat of formation (ΔH) against the reaction co-ordinate θ (Figure 1) for the pericyclic conversion of (14) into (15)

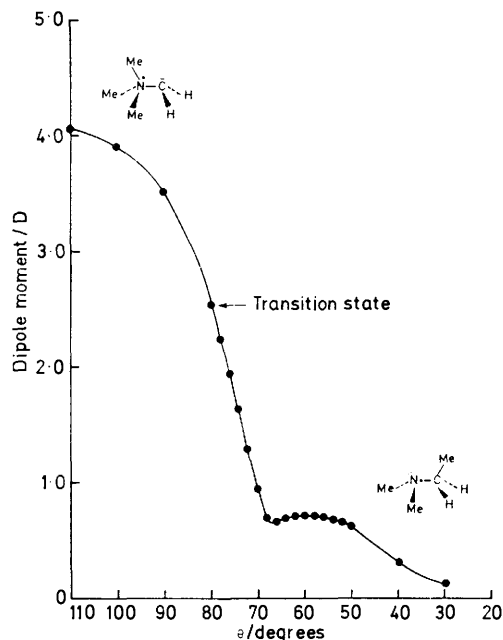


FIGURE 4 Plot of the calculated dipole moment (μ) vs. θ for the pericyclic conversion of (14) into (15). The arrow indicates the position of the transition state

Figure 4 shows the variation of dipole moment (μ) during the reaction as a function of the reaction co-ordinate θ . The arrow indicates the position of the transition state.

¹² M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 1971, **93**, 4290, 4291, 4292.

¹³ U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Letters*, 1969, 3415.

DISCUSSION

The results reported above obviously provide strong support for the suggestion that antiaromatic pericyclic reactions may occur very readily if they are sufficiently exothermic. The calculated activation energy for conversion of (14) into (15) in the gas phase is extremely small (17 kJ mol⁻¹) although this is an antiaromatic process violating the Woodward-Hoffmann rules.

While the Stevens rearrangement was chosen simply as a convenient example of an extremely exothermic reaction that could take place by an antiaromatic pericyclic pathway, it is also of interest in view of current controversy concerning its mechanism. The observation of the CIDNP effect during a number of Stevens rearrangements has led to the suggestion that the reactions may not in fact be pericyclic but take place by fission to an intermediate pair of radicals [(9) \rightarrow (13)] which then recombine inside a solvent cage.^{13,14} This evidence certainly shows that at least some of the product must have been formed by recombination of radicals but does not establish this as the main reaction path. The CIDNP effect is so sensitive that large signals can be obtained in cases where only a few percent of product are formed *via* radicals.

The calculations reported here suggest that the Stevens rearrangement may very well take place by a concerted pericyclic path but does not allow a distinction between this and the radical pair mechanism. In the case of (14), MINDO/3 predicts dissociation to radicals ($\text{Me}_2\text{NCH}_2\cdot + \cdot\text{CH}_3$) to be exothermic ($\Delta H_2 = 42$ kJ mol⁻¹). In the gas phase (14) should then dissociate without activation. In practice, however, the Stevens rearrangement is carried out in polar solvents where the heat of solvation of the zwitterionic ylide may well be 125–175 kJ mol⁻¹. Most of this solvation energy will be lost on forming the pair of weakly polar radicals and the energy required for their formation will be correspondingly increased. On the other hand the transition state for the pericyclic reaction, while less polar than the ylide, should still be strongly polar since it should be nearer to the reactant ylide than to the product in structure. The increase in activation energy on passing from the gas phase to a polar solvent should then be much less than that for fission to radicals. Our calculations do indeed indicate that the transition state for the conversion of (14) into (15) (see Figure 2) is much closer to (14) than to (15) in structure and Figure 4 shows that its calculated dipole moment (2.5 D), while less than that of (14) (4.0 D), is still large. The pericyclic path could therefore very well be favoured for the reaction of (14) in polar solvents.

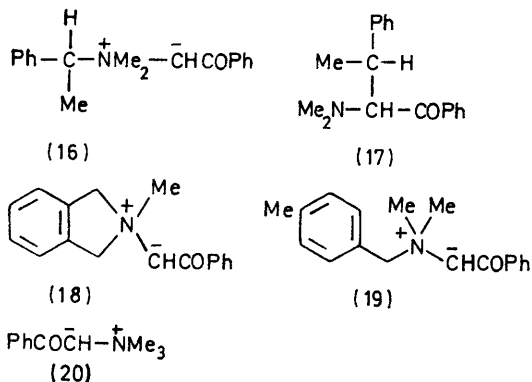
Little is known concerning the conversion of (14) into (15). Wittig and Polster reported the preparation of (14) by treating tetramethylammonium bromide with phenyl-lithium.¹⁵ The product was, however, isolated

¹⁴ R. W. Jemison, S. Mageswaran, W. D. Ollis, S. E. Potter, A. J. Pretty, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Comm.*, 1970, 1201.

¹⁵ G. Wittig and R. Polster, *Annalen*, 1956, **599**, 1.

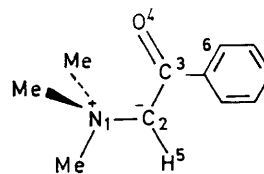
as a complex with lithium bromide and may have been an alkyl-lithium derivative, $\text{LiCH}_2\text{NMe}_3\text{Br}^-$. When a mixture of phenyl-lithium and phenylsodium was used, the ylide decomposed giving (15) in 49% yield.¹⁶ In a study of the decomposition of tetramethylammonium fluoride by potassium amide, Musker found that (15) was formed in 5–10% yield.¹⁷

The majority of Stevens rearrangements reported in the literature have involved ylides stabilized by +E substituents, usually acyl. We have not studied such a process because the molecules in question are rather large and the cost of following their rearrangements by the SIMPLEX method would be excessive. It has been reported that Stevens rearrangement of the ylide (16) to (17) in chloroform takes place with 95% retention of configuration.¹⁸ The high degree of stereospecificity certainly seems to suggest that at least a large part of the reaction may have taken place by the pericyclic route.



The bonding in nitrogen ylides is of interest in view of the large separation of charge in them and because the structures of the stable ylides [(18) and (19)] have recently been determined by X-ray crystallography.¹⁹ For comparison we have calculated the structure of the benzoyl derivative (20) of (14). The calculated structure is shown in Figure 5 together with the measured lengths of corresponding bonds in (18) and (19). In order to reduce the amount of computation, the benzene ring in (20) was assumed to have the structure calculated (MINDO/3) for benzene. Note that the predicted length of the $\text{CH}-\text{CO}$ bond in (20) is much greater, and that of the $\text{C}-\text{O}$ bond much less, than the measured length of corresponding bonds in (18) or (19). Evidently the negative charge is much more strongly localized on the ylide CH in our calculated structure than in (18) or (19), the latter approximating closely to enolates ($\text{N}^+-\text{CH}=\text{C}^--\text{O}$). Likewise we predict the N^+-C bond to be shorter in (20) than the corresponding bonds in (18) or (19), as would be expected if the carbon atom carries

a large negative charge. Our calculations of course refer to an isolated molecule in the gas phase where the

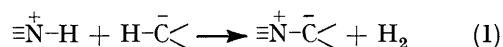


$\overline{12}$	= 1.457 (1.48; 1.47)
$\overline{23}$	= 1.417 (1.36; 1.34)
$\overline{34}$	= 1.234 (1.27; 1.30)
$\overline{25}$	= 1.109
$\overline{36}$	= 1.543 (1.52; 1.51)
$\overline{123}$	= 129.2 (119.0; 123.0)
$\overline{234}$	= 123.0
$\overline{523}$	= 121.5
$\overline{1234}$	= 0.1
$\overline{5234}$	= 180.0

FIGURE 5. Calculated bond lengths (\overline{rs}) (Å) and bond angles (\overline{rst}) (°) in (20). The first value in parentheses is the observed value for the corresponding bond or angle in (18), the second for that in (19).

energy of the enolate structure would be increased by the large separation of charge in it (*cf.* N^+-CH^- with $\text{N}^+-\text{CH}=\text{C}^--\text{O}$). The ylide molecules in a crystal of ylide are in a highly polar environment where the effect of charge separation must be much less than in the gas phase.

A rough estimate of the electrostatic energy due to charge separation can be made by considering the change in energy when an ylide is formed by union of an ammonium ion with an anion:



The change in energy (ΔE) can be written in terms of bond energies (E_{XY}) and the electrostatic energy (E^{+-}):

$$\Delta E = E_{\text{NH}} + E_{\text{CH}} - E_{\text{CN}} - E_{\text{HH}} + E^{+-} \quad (2)$$

If bond energies followed an arithmetic mean rule, the bond energy of an XY bond being the mean of the bond energies of XX and YY, the bond energy term ($E_{\text{NH}} + E_{\text{CH}} - E_{\text{CN}} - E_{\text{HH}}$) in equation (2) would vanish. Its actual value can therefore be estimated by using Pauling's rule²⁰ for deviations from the arithmetic mean, *i.e.*

$$E_{\text{XY}} = 0.5(E_{\text{XX}} + E_{\text{YY}}) + (\alpha_{\text{X}} - \alpha_{\text{Y}})^2 \quad (3)$$

where α_{X} and α_{Y} are the electronegativities of X and Y. Using the electronegativity values suggested by Jolly,²¹ we estimate the value of the bond energy term in equation (2) to be *ca.* 0.25 eV.

¹⁹ N. A. Bailey, S. E. Hull, G. F. Kersting, and J. Morrison, *Chem. Comm.*, 1971, 1429.

²⁰ L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn. Cornell University Press, Ithaca, New York, 1960.

²¹ W. L. Jolly, *J. Amer. Chem. Soc.*, 1970, **92**, 3260.

¹⁶ G. Wittig and D. Krauss, *Annalen*, 1964, **679**, 34.

¹⁷ W. K. Musker, *J. Org. Chem.*, 1967, **32**, 3189.

¹⁸ J. H. Brewster and M. W. Kline, *J. Amer. Chem. Soc.*, 1952, **74**, 5179.

The Table shows total energies for the various species calculated using MINDO/3. Using these and equations

Total energies of various species calculated by MINDO/3

Species	Electronic energy (eV)
$\text{Me}_3\text{N}^+\text{H}^-$	-712.87
CH_3^-	-168.59
PhCOCH_2^-	-1427.87
H_2	-31.72
$\text{Me}_3\text{N}^+\text{CH}_2^-$	-858.01
$\text{Me}_3\text{N}^+\text{CHCOPh}^-$	-2115.11

(2) and (3) we arrive at the following estimates of the electrostatic energies E^{+-} in (14) and (20): (14) $E^{+-} = 8.0$ eV (770 kJ mol⁻¹), (20) $E^{+-} = 6.1$ eV (590 kJ mol⁻¹).

The electrostatic energies are both very large and that for (20) is significantly less than that for (14). One would of course expect the electrostatic energies to be large since both compounds, according to simple valence theory, are zwitterionic. One would also expect the electrostatic energy to be less for (20) than for (14) because in (20) the negative charge is dispersed over the enolate system. The mean distance between the positive and negative charges is consequently greater than it is in (14) and the electrostatic energy ($-e^2/r$) correspondingly less.

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