Conclusions

The main conclusion from the results described in this paper, and the preceding one,[1] is that the treatment described here provides an astonishingly good account of the heats of formation and geometries of conjugated molecules. Indeed, it seems likely that the calculated heats of formation are subject to smaller errors than any but the most recent thermochemical measurements; the present procedure should therefore provide a satisfactory and very simple substitute for experiment in determining heats of formation of conjugated and aromatic systems. Calculations of this kind should be of especial interest to biochemists, in view of the bio-logical importance of such compounds; the procedures developed here should prove invaluable in interpreting their chemical properties. Previous attempts in this direction have been limited to the HMO method, which is known to be unreliable for molecules containing heteroatoms, or to SCF treatments in which the parameters were chosen by reference to spectroscopic data. The calculations can of course be carried out in a fraction of the time, and at much less cost, than corresponding measurements of heats of combustion: it should be added that an improved version of our computer program, written by Mr. J. A. Hashmall, is available from The Quantum Chemistry Program Exchange (for details see part XI[1]).

Ground States of Conjugated Molecules.[1] XIII. Basicities of Conjugated Carbonyl Compounds[2]

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Abstract: The completely self-consistent treatment of heteroconjugated molecules derived in part XII[1] has been applied to a wide variety of conjugated carbonyl compounds and the conjugated acids derived from them, and the results have been used to account for the pK_a of the carbonyl compounds. The correlation given by the present method is much superior to those derived from the less refined treatments used previously.

Previous papers[1,4] of this series have described an improved SCF–MO treatment of conjugated molecules; our present objective is to test the validity of this approach by applying it to a wide range of chemical problems. Here we describe one such application, an interpretation of the relation between structure and basicity in a series of conjugated carbonyl compounds. This long-standing problem provides a good touchstone for chemical theories for several reasons. First, there are extensive data for the basicities of such compounds, covering a wide range of structural variation. Secondly, the observed dissociation constants cover a wide range. Thirdly, the quantities to be predicted are equilibrium constants rather than rate constants; rate constants are harder to interpret since their prediction involves unavoidable assumptions concerning the geometries of transition states.

The basic strength of a given carbonyl compound, R_2CO, is determined by the difference in free energy between it and its conjugate acid R_2COH^+. Making the usual assumption[5] that the differences in basicity are due to changes in the energy (ΔE) rather than the entropy of reaction, we find that the equilibrium con-stant (K) for a given carbonyl compound should be given by

$$-RT \log K = C + \Delta E \qquad (1)$$

where C is a constant. A plot of $\log K$ against ΔE should then be a straight line.

Making the Hückel approximation of treating σ and π electrons independently, we can write ΔE in the form

$$\Delta E = \Delta E_{\sigma b} + \Delta E_{\pi b} \qquad (2)$$

where $\Delta E_{\sigma b}$ and $\Delta E_{\pi b}$ are the differences in σ- and π-binding energy, respectively, between the carbonyl compound and its conjugate acid. Previous workers have further assumed that $\Delta E_{\sigma b}$ is the same for different carbonyl compounds, their relative basicities being determined solely by the π-energy term $\Delta E_{\pi b}$; in this case, a plot of $\log K$ vs. $\Delta E_{\pi b}$ should be linear, $\Delta E_{\pi b}$ being calculated by some appropriate theoretical treatment.

Culbertson and Pettit[6] applied this relation to a number of aldehydes (ArCHO), ArH being an al-ternant aromatic hydrocarbon. They pointed out that in the conjugate acid $ArCHOH^+$, the positive charge should reside mainly on carbon rather than on the elec-tronegative oxygen; the π-MO's of $ArCHOH^+$ should then resemble those of the corresponding arylcarbo-nium ion $ArCH_2^+$, and $\Delta E_{\pi b}$ should be approximately equal to the difference in π-binding energy between ArH and $ArCH_2^+$. They found an excellent correlation be-tween the measured basic dissociation constants and

(1) Part XII: M. J. S. Dewar and T. Morita, J. Am. Chem. Soc., 91, 796 (1969).

(2) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(3) Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Japan.

(4) M. J. S. Dewar and C. de Llano, J. Am. Chem. Soc., 91, 789 (1969).

(5) See, e.g., M. J. S. Dewar, Advan. Chem. Phys., 8, 65 (1965).

(6) G. Culbertson and R. Pettit, J. Am. Chem. Soc., 85, 741 (1963).

such differences in π energy, which they calculated by the PMO method.[7] This treatment has of course obvious limitations. Apart from the crudity of the method used to estimate $\Delta E_{\pi b}$, it can be applied only to alternant systems; moreover the reported correlation referred only to one series of compounds of very similar type.

Kende[8] has recently discussed a much wider range of carbonyl compounds, both alternant and nonalternant, and including both aldehydes and ketones. He found a satisfactory correlation between the observed basic dissociation constants and the differences in *total* π energy between the carbonyl compounds and their conjugate acids. These differences were calculated by a Pariser–Parr–Pople method, assuming all C–C bonds to have a common length of 1.40 Å, and using values of 1.23 and 1.38 Å, respectively, for the length of the CO bond in each carbonyl compound, and in its conjugate acid.

Although the correlation found by Kende was good, his treatment is open to serious criticism. In the first place, $\Delta E_{\pi b}$ in eq 2 is a difference in π-*binding* energy not *total* π energy; the neglect of core repulsion in Kende's treatment is therefore unjustified.[9] Secondly, the assumption of a common bond length for all C–C bonds is unrealistic; in many of the compounds considered by Kende there must in fact be a strong alternation in length between "single" and "double" CC bonds. Thirdly, the bond lengths in a given carbonyl compound must often differ markedly from those in the conjugate acid; Kende makes no allowance for the effects of this on either the σ- or the π-binding energy.

Here we report a general treatment of this problem in terms of our improved SCF–MO treatment[1] of hetero-conjugated systems, making allowance for the effects of changes in molecular geometry with protonation on the binding energies of both σ and π electrons.

Theoretical Method

The calculations were carried out by the method described in the preceding paper,[1] in which allowance is made for the effect of changes in bond length both on the integrals used to calculate the π-binding energy and on the bond energies of σ bonds. The necessary parameters had already been determined,[1] with one exception, *viz.*, the polarization of σ bonds formed by a positively charged trigonal oxygen atom. Assuming the same proportionality between σ polarization and electronegativity difference (*i.e.*, eq 16 of part XII[1]), we found values for the formal charges due to σ polarization in the conjugate acid from a carbonyl compound (eq 3). The

$$\begin{array}{c} +0.22e \quad +0.19e \\ >\text{C}{=}\text{O}{-}\text{H} \\ -0.14e \end{array} \tag{3}$$

corresponding changes in the one-center integrals for oxygen, and for the adjacent carbon atom, were again found by the method of part XII (eq 17, with the parameters for trigonal oxygen from Table V). The values found in this way for protonated carbonyl are shown in

(7) M. J. S. Dewar, *J. Am. Chem. Soc.*, **84**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).
(8) A. Kende, *Advan. Chem. Phys.*, **8**, 133 (1965).
(9) M. J. S. Dewar and C. C. Thompson, *J. Am. Chem. Soc.*, **87**, 4414 (1965).

Table I, together with values for neutral carbonyl and carbon, taken from part XII.[1]
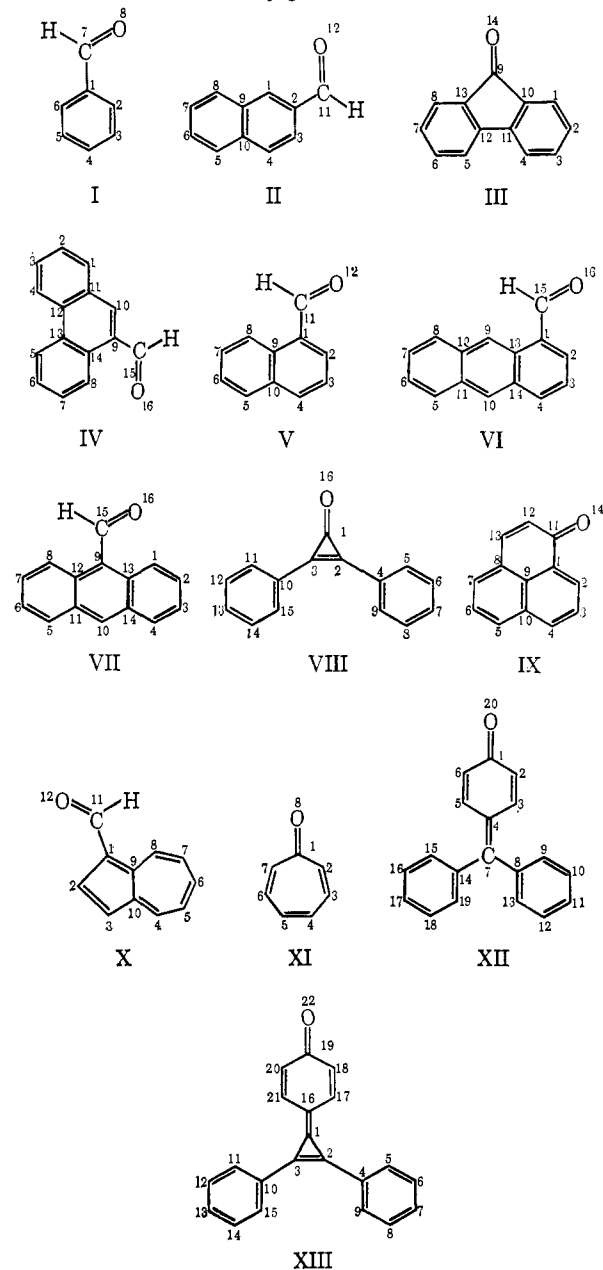
Results

Table II shows values for $E_{\pi b}$ and $E_{\sigma b}$ for the carbonyl compounds listed in Chart I, and for the conjugated acids derived from them. The penultimate column

Table I. Parameters Used in π Calculations for Carbonyl Compounds and Their Conjugate Acids

Atom	Core charge, e	W, eV	(ii,ii), eV	Z
C in C=O	1.10	−12.2872	11.6786	3.34
O in C=O	0.90	−16.0190	14.4871	3.98
C in C=ÖH	1.22	−13.6733	12.3197	3.52
O⁺ in C=ÖH	1.59	−26.7969	16.5367	4.83
Other C	1.00	−11.1600	11.1300	3.18

Chart I. Geometries of Conjugated Ketones

Table II. Energy Terms from SCF–MO Calculations[a]

Molecule	Unprotonated species		Protonated species		ΔE	pK_a
	$E_\pi b$	$E_\sigma b$	$E_\pi b$	$E_\sigma b$		
Benzaldehyde (I)	12.3730	29.6405	13.2122	29.8523	0.0000	−6.99
2-Naphthaldehyde (II)	18.3446	48.2708	19.3226	48.5073	−0.1635	−6.68
Fluorenone (III)	21.4890	59.6095	22.7235	59.8715	−0.4455	−6.65
9-Phenanthraldehyde (IV)	24.3801	66.9460	25.4540	67.2252	−0.3021	−6.34
1-Naphthaldehyde (V)	18.3458	48.2786	19.3565	48.5596	−0.2407	−6.34
1-Anthraldehyde (VI)	24.1165	66.9301	25.2256	67.2432	−0.3712	−5.71
9-Anthraldehyde (VII)	24.1322	66.9342	25.4919	67.2428	−0.6172	−4.81
Diphenylcyclopropenone (VIII)	23.4722	66.9093	26.1128	67.1225	−0.8028	−3.20
Perinaphthenone (IX)	21.2952	59.5360	22.7911	59.9148	−0.8237	−1.40
Azulene-1-aldehyde (X)	17.0968	48.4786	18.8837	48.5721	−0.8293	−1.00
Tropone (XI)	11.7402	29.4650	13.0068	29.7965	−0.5471	−0.60
Fuchsone (XII)	29.3823	81.4823	31.2298	81.9693	−1.2835	1.70
Diphenylquinocyclopropene (XIII)	32.4369	92.8186	34.9102	93.2138	−1.8176	5.00

[a] Measured in electron volts.

Table III. Calculated Bond Lengths, Å

Molecule[a]	Bond[a]	Un-protonated species	Protonated species	Molecule[a]	Bond[a]	Un-protonated species	Protonated species
Benzaldehyde (I)	1–2	1.399	1.424	1-Naphthaldehyde (V)	1–2	1.380	1.422
	2–3	1.398	1.388		2–3	1.421	1.394
	3–4	1.394	1.401		3–4	1.374	1.396
	4–5	1.399	1.406		4–10	1.429	1.419
	5–6	1.392	1.383		5–6	1.374	1.378
	1–6	1.404	1.427		6–7	1.422	1.416
	1–7	1.465	1.411		7–8	1.374	1.384
	7–8	1.252	1.300		8–9	1.426	1.412
2-Naphthylaldehyde (II)	1–2	1.379	1.415		9–10	1.403	1.411
	2–3	1.428	1.445		1–9	1.432	1.445
	3–4	1.371	1.365		5–10	1.427	1.426
	4–10	1.430	1.435		1–11	1.463	1.402
	5–6	1.374	1.381		11–12	1.253	1.307
	6–7	1.422	1.421	1-Anthraldehyde (VI)	1–2	1.373	1.422
	7–8	1.374	1.374		2–3	1.432	1.395
	8–9	1.427	1.432		3–4	1.366	1.395
	9–10	1.403	1.418		4–14	1.440	1.421
	1–9	1.427	1.405		5–6	1.365	1.368
	5–10	1.426	1.416		6–7	1.434	1.429
	2–11	1.464	1.405		7–8	1.366	1.371
	11–12	1.253	1.305		8–12	1.439	1.430
Fluorenone (III)	1–2	1.399	1.402		9–12	1.404	1.415
	2–3	1.394	1.390		9–13	1.400	1.388
	3–4	1.399	1.412		10–11	1.403	1.403
	4–11	1.396	1.384		10–14	1.401	1.408
	1–10	1.396	1.405		1–13	1.444	1.453
	10–11	1.406	1.422		5–11	1.440	1.437
	11–12	1.470	1.474		13–14	1.417	1.429
	9–10	1.472	1.438		11–12	1.415	1.417
	9–14	1.255	1.309		1–15	1.463	1.397
9-Phenanthraldehyde (IV)	1–2	1.380	1.374		15–16	1.253	1.311
	2–3	1.413	1.420	9-Anthraldehyde (VII)	1–2	1.366	1.384
	3–4	1.381	1.382		2–3	1.434	1.434
	4–12	1.416	1.413		3–4	1.365	1.365
	5–6	1.382	1.385		4–14	1.440	1.440
	6–7	1.412	1.408		1–13	1.438	1.438
	7–8	1.382	1.388		13–14	1.417	1.417
	8–14	1.416	1.408		9–13	1.407	1.407
	9–10	1.369	1.415		10–14	1.400	1.400
	10–11	1.440	1.405		9–15	1.461	1.461
	11–12	1.401	1.419		15–16	1.254	1.254
	12–13	1.447	1.441		5–6	1.367	1.376
	13–14	1.401	1.407		5–11	1.438	1.429
	9–14	1.446	1.455		6–7	1.432	1.417
	5–13	1.416	1.414		7–8	1.367	1.384
	1–11	1.418	1.433		8–12	1.436	1.412
	9–15	1.466	1.401		9–12	1.410	1.443
	15–16	1.252	1.307		10–11	1.406	1.412
					11–12	1.414	1.415

Table III (Continued)

Molecule[a]	Bond[a]	Un-protonated species	Protonated species	Molecule[a]	Bond[a]	Un-protonated species	Protonated species
Diphenylcyclopropenone (VIII)	1–2	1.452	1.413	Tropone (XI)	1–2	1.463	1.422
	2–3	1.366	1.403		2–3	1.355	1.380
	2–4	1.466	1.449		3–4	1.453	1.425
	4–5	1.401	1.407		4–5	1.357	1.377
	5–6	1.395	1.392		1–8	1.259	1.318
	6–7	1.397	1.399	Fuchsone (XII)	1–2	1.465	1.418
	7–8	1.397	1.399		2–3	1.352	1.380
	8–9	1.395	1.392		3–4	1.460	1.425
	4–9	1.401	1.407		4–7	1.367	1.415
	1–16	1.264	1.323		7–8	1.463	1.440
Perinaphthenone (IX)	1–2	1.380	1.408		8–9	1.400	1.410
	2–3	1.422	1.403		9–10	1.396	1.391
	3–4	1.373	1.387		10–11	1.396	1.399
	4–10	1.429	1.422		11–12	1.398	1.400
	5–6	1.377	1.387		12–13	1.394	1.391
	6–7	1.417	1.403		8–13	1.402	1.410
	7–8	1.383	1.404		1–20	1.258	1.326
	8–9	1.427	1.420	Diphenylquinocyclopro-propene (XIII)	1–2	1.452	1.415
	9–10	1.404	1.413		2–3	1.369	1.401
	1–9	1.430	1.427		2–4	1.465	1.452
	1–11	1.465	1.429		4–5	1.401	1.406
	5–10	1.424	1.421		5–6	1.395	1.393
	8–13	1.462	1.436		6–7	1.397	1.398
	11–12	1.466	1.420		7–8	1.397	1.398
	12–13	1.351	1.377		8–9	1.395	1.393
	11–14	1.259	1.320		4–9	1.401	1.406
Azulene-1-aldehyde (X)	1–2	1.411	1.443		1–16	1.375	1.435
	2–3	1.388	1.372		16–17	1.456	1.417
	3–10	1.413	1.426		17–18	1.354	1.384
	4–5	1.401	1.392		18–19	1.462	1.414
	5–6	1.395	1.406		19–22	1.261	1.330
	6–7	1.405	1.396				
	7–8	1.392	1.402				
	8–9	1.411	1.400				
	9–10	1.460	1.431				
	1–9	1.407	1.443				
	4–10	1.403	1.413				
	1–11	1.458	1.389				
	11–12	1.355	1.313				

[a] Structures and numbering shown in Chart I.

gives the difference in total energy (ΔE) between the two species, relative to that for benzaldehyde, while the last column lists the experimental values for pK_a quoted by Kende.[8]

Discussion

If eq 1 holds, a plot of pK_a vs. ΔE should be a straight line of slope $-(2.303RT)^{-1}$, or -16.7 eV^{-1} for $T = 298°K$. Figure 1 shows this plot for the data listed in Table II. It will be seen that the points do lie close to a straight line, the correlation coefficient (0.94) being considerably greater than that (0.90) for Kende's[8] plot, but the slope of the line (-7.21 eV^{-1}) is less than half the theoretical value. A discrepancy in this direction would however be expected, as the following argument shows.

Equation 1 was derived[5] on the understanding that solvation effects are the same throughout the series of compounds under consideration, the corresponding contributions being consequently incorporated in the constant C in eq 1. This contribution represents the difference in energy of solvation between a neutral carbonyl compound and the positively charged conjugate acid derived from it. Since the solvation energies of neutral molecules are relatively small, it is reasonable to assume that differences in solvation energy between

different neutral carbonyl compounds may be negligible. This, however, cannot be the case for the large ionic solvation energies of the corresponding conjugate acids; here the solvation energy will vary greatly with the extent to which the charge is dispersed over the con-
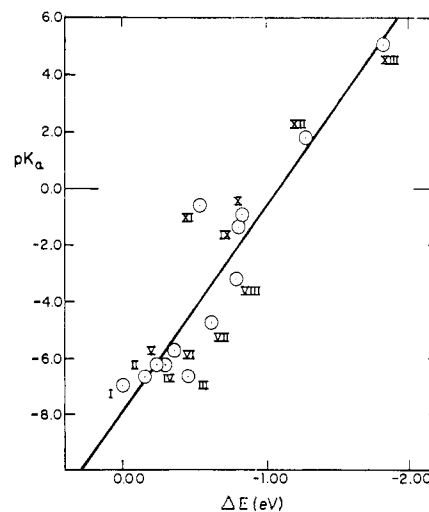

Figure 1. Plot of pK_a vs. ΔE for the carbonyl compounds in Chart I.
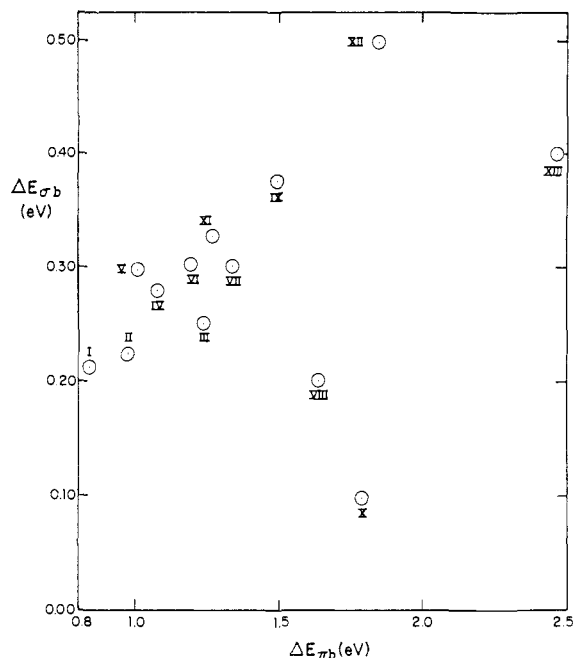
Figure 2. Plot of $\Delta E_{\sigma b}$ vs. $\Delta E_{\pi b}$ for the compounds listed in Chart I.

jugated system in the ion. The dispersion of charge should as a rule be greater, and the solvation energy correspondingly less, the greater the resonance energy of the conjugated ion; this in turn will be greater, the greater pK_a. Consequently the more stable the conjugate acid of a given carbonyl compound, the more will solvation hinder protonation of the latter; solvation will therefore tend to reduce the over-all spread of pK_a in a series of compounds of this type, thus reducing the slope of the plot in Figure 1.

It was pointed out in the introduction that ΔE in eq 1 must refer to the difference in *total* energy between reactants and products in a reversible reaction, not to the difference in π-binding energy ($\Delta E_{\pi b}$) or "resonance energy." A linear relationship between log K and $\Delta E_{\pi b}$ could hold only if the corresponding difference ($\Delta E_{\sigma b}$) in σ-binding energy were the same for each reaction, or if there were a linear relation between $\Delta E_{\sigma b}$ and $\Delta E_{\pi b}$. Figure 2 shows a plot of $\Delta E_{\sigma b}$ vs. $\Delta E_{\pi b}$ for the compounds listed in Chart I, the values being taken from Table II. Obviously $\Delta E_{\sigma b}$ is by no means constant, nor is there a linear relation between $\Delta E_{\sigma b}$ and $\Delta E_{\pi b}$. On the other hand the values for $\Delta E_{\sigma b}$ for the alternant aldehydes I–VII are very similar; this presumably is the reason why Culbertson and Pettit got such good results from their PMO treatment, which was limited to compounds of this type.

Bond Lengths

In the course of these calculations, bond lengths were automatically computed; these are listed in Table III, both for the carbonyl compounds and for their conjugate acids.

Unfortunately no accurate structure determinations are available for comparison with those predictions. Kimura, et al.,[10] have studied tropone by electron diffraction and claim that the ring in it forms a regular heptagon with bond lengths of 1.405 Å; this does not agree with our calculations which predict a marked alternation of bond lengths. However the limits of error given by Kimura, et al., were large (± 0.04 Å), and a symmetrical structure seems in any case to be ruled out by other evidence; it would imply that tropone has a zwitterionic structure approximating closely to $C_7H_6{}^+$–O^-, a conclusion inconsistent with the measured dipole moment and infrared spectrum. Measurements have also been reported by Trotter[11] for 9-anthraldehyde; these agree qualitatively with our calculations but the reported limits of experimental error are again too large to make the comparison very meaningful.

(10) K. Kimura, S. Suzuki, M. Kimura, and M. Kubo, Bull. Chem. Soc. Japan, 31, 1051 (1958).
(11) J. Trotter, Acta Cryst., 12, 922 (1959).