Table I. Relative Intensities of Selected Ions[a]

	$C_6H_5CH_2CO_2CH_2C_6H_5$ (I)	$C_6H_5CD_2CO_2CD_2C_6H_5$[b] (II)	$C_6H_5CH_2CO_2CD_2C_6H_5$[b] (III)	$C_6H_5CD_2CO_2CH_2C_6H_5$[b] (IV)
$M\cdot^+$	100[c]	100[c]	100[c]	100[c]
$C_7H_5D_2$		324	196	102
$C_7H_6D_1$		21.7	8.4	14.6
C_7H_7	319	13.0	110	191
$C_5H_3D_2$		18.7	9.12	6.99
$C_5H_4D_1$		20.1	9.98	8.25
C_5H_5	41.4	8.1	21.1	21.2

[a] Corrected for ^{13}C contributions. [b] II was found to be 88.8 atom % d_4, 9.5 atom % d_3, and 1.7 atom % d_2; III was found to be 97.7 atom % d_2 and 2.3 atom % d_1; IV was found to be 95.4 atom % d_2 and 4.6 atom % d_1 by low-voltage mass spectrometry. [c] Total ion intensity for all molecular ions, including partially deuterated molecular ions.

Meyerson[7] for bibenzyl-α,β-d_4 ($d_2 = 0.40$; $d_1 = 0.43$; $d_0 = 0.165$), which is thought to experience complete H–D randomization in the decomposition of the tropylium ion. However, a tropylium ion formed by random insertion should produce the $C_5H_5^+$, $C_5H_4D^+$, and $C_5H_3D_2^+$ ions in the ratio 0.47:0.47:.047 for II, values substantially different from those found (0.40:0.43:0.17).

To better visualize what the data may mean, the isotopic distributions of $C_5H_5^+$ ions from $C_7H_7^+$ ions were calculated assuming that the $C_7H_7^+$ ions from eq 1 and 2 are similar in structure and have completely randomized H–D prior to loss of acetylene. The results of these calculations, expressed as observed/calculated ratios, are given in Table II.

Table II. Observed/Calculated Ratios for Distribution of Deuterium in C_5 Ions[a]

	II	III	IV
d_2	0.93	0.76	1.22
d_1	0.91	0.78	1.18
d_0	1.79	1.36	0.90

[a] A referee has suggested this form for presentation of data.

The data are clearly inconsistent with complete randomization of H–D within the decomposing "C_7H_7" ions. Indeed, the scrambling results are not consistent with C_7 models of benzyl-α-d_2, tropylium-*1,2*-d_2, or norcaradienyl-d_2, if equal rates of decomposition and similar structure of the two C_7 moieties are assumed.

The ratios in Table II likewise indicate that the C_7 ions derived from the benzyloxy grouping decompose less readily than those formed from the phenylacetate benzyl portion. This result, in part, may account for the greater intensity of the C_7 ion formed by benzyl–oxygen bond cleavage.

The apparent difference in the rate of decomposition of the C_7 ions is most readily explainable if the reactive C_7 ions formed by the two processes are structurally different. The labeled benzyl phenylacetates thus represent the first case in which decomposing $C_7H_7^+$ ions have not attained an equilibrated energy manifold on the normal ion time scale.[10] Further studies to elucidate the exact structure of the two C_7H_7 ions include ion kinetic energy measurements and low-voltage spectra will be presented in the full paper.

Acknowledgment. Acknowledgment of financial support of this work is made to the Kansas State University Bureau of General Research and (by J. C. W.) to the National Science Foundation Undergraduate Research Participation Program, Kansas State University, summer, 1972.

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[10] An ion kinetic energy study of isomeric C_7H_7 methyl ethers indicates equilibrium to a common structure occurs in the formation of the $C_7H_7^+$ ion. $C_7H_7^+$ ions which react further, however, may do so from structurally different forms on the metastable time scale: R. G. Cooks, M. Bertrand, and M. K. Hoffman, manuscript in preparation.

Geometrical Reaction Coordinates.[1] II. Nucleophilic Addition to a Carbonyl Group

Sir:

In the course of a survey of crystal-structure analyses of compounds containing nucleophilic groups and electrophilic centers we have discovered some structural regularities which, we believe, provide an experimental basis for mapping the reaction coordinate (minimum energy pathway) for the addition reaction of a nucleophile to a carbonyl group. The observed distance between nucleophile (N:) and carbonyl carbon ranges, in the examples studied, from about 1.5 Å (covalent bonding) to 3 Å; the longer distances have sometimes been interpreted as evidence for nonbonded interactions of donor–acceptor or dipole–dipole type. We take the view that each example can be regarded as a case where the addition reaction has proceeded to a greater or lesser extent but has been frozen in at a certain stage by the intra- or intermolecular constraints imposed by the crystal environment. Each case then provides a sample point on or close to the reaction coordinate, and a sufficiently large number of points should map out the reaction coordinate, provided that the perturbations from the different crystal and molecular environments can be averaged out. Similar arguments[1,2] have been used to derive the minimum energy pathway for the nucleophilic substitution reactions $I^- + I{-}I \rightarrow [I\cdots I\cdots I]^- \rightarrow I{-}I + I^-$ and $X + CdS_3Y \rightarrow [X\cdots CdS_3\cdots Y] \rightarrow XCdS_3 + Y$. In this communication we present results for the addition of an amino group to a carbonyl or, equivalently, for the reverse elimination process.

Structural parameters for intramolecular $N\cdots C{=}O$

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[1] Part I: H. B. Bürgi, *Inorg. Chem.*, in press.

[2] H. Bent, *Chem. Rev.*, **68**, 587 (1968).

Table I. Experimental Structural Parameters for N···C═O Interactions[a,b]

Compound	l_1[c]	l_2[c]	d_1	d_2	Δ	α[c]	β_1	β_2	β_3	β_4	γ[c]	Ref
A, methadone	1.510	1.554	2.910	1.214	0.064	105.0	119.7	122.2	89.7	82.7	117.5	4a
B, cryptopine	1.521	1.515	2.581	1.209	0.102	102.2	121.2	119.0	85.0	95.2	118.1	4b
C, protopine	1.520	1.505	2.555	1.218	0.115	101.6	120.8	120.0	84.7	97.7	117.2	5
D, clivorine	1.508	1.546	1.993	1.258	0.213	110.2	118.9	115.7	92.0	93.6	118.8	6
E, retusamine	1.49	1.56	1.64	1.38	0.36	110.9	115.7	107.0	101.4	100.1	120.2	7
F, *N*-brosylmitomycin A	1.56	1.56	1.49	1.37	0.42	113.7	103.6	113.6	102.0	103.9	119.9	8

[a] For a definition of symbols see Figure 1. [b] Distances in ångströms, angles in degrees; $\sigma(l) \sim \sigma(d) \leq 0.02$ Å; $\sigma(\alpha) \sim \sigma(\beta) \sim \sigma(\gamma) \leq 1.3°$. [c] $\langle l_i \rangle = 1.529$ Å, $\langle \alpha \rangle = 107.3\ (5.0)°$, $\langle \gamma \rangle = 118.6\ (1.2)°$.

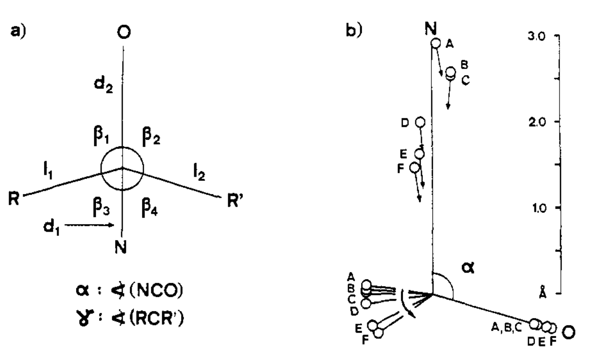

Figure 1. (a) Definition of symbols. (b) Reaction coordinate projected on the NCO plane showing nitrogen (top, arrows indicate the estimated direction of the lone pair), carbonyl oxygen (bottom right), and bisector of γ (RCR′) (bottom left).

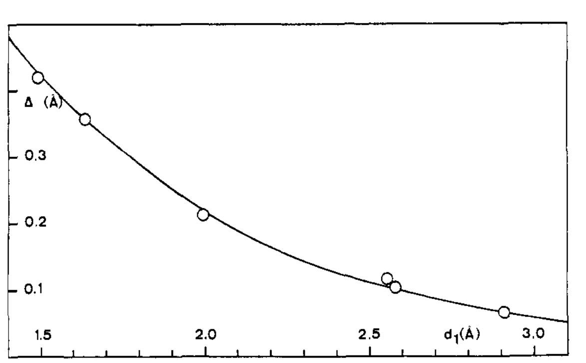

Figure 2. Correlation plot of Δ *vs.* d_1 (smooth curve obtained from eq 1).

interactions[3] (Figure 1a) obtained from six crystal-structure analyses[4–8] are summarized in Table I. In all cases the N, C, and O atoms lie in an approximate local mirror plane (m) but the C atom deviates significantly from the plane defined by R, R′, and O; the amount of this deviation (Δ) increases as the C···N distance (d_1) decreases. From Figure 2 it is seen that the experimental points lie close to the smooth curve

$$d_1 = -1.701 \log \Delta + 0.867 \text{ Å} \qquad (1)$$

where the constants were found by least-squares analysis. Extrapolation to $d_1 = 1.479$ Å, the standard C–N bond length,[9] leads to $\Delta_{\max} = 0.437$ Å and eq 1 can be rewritten as

$$d_1 = -1.701 \log n + 1.479 \text{ Å} \qquad (2)$$

with $n = \Delta/\Delta_{\max}$. A similar equation (3) can be given

$$d_2 = -0.71 \log (2 - n) + 1.426 \text{ Å} \qquad (3)$$

for the C–O distances; here the multiplicative constant is taken from Pauling's equation relating C–C bond length and bond number,[10] and the additive constant is the standard C–O bond distance.[9] Equations 2 and 3 reproduce the observed distances d_1 and d_2 with a mean deviation of 0.03 Å and hence imply that the sum of the C–O and C–N bond numbers equals two for all the structures under discussion.

It is difficult to detect any systematic trend in the angles α and γ, which do not vary by more than a few degrees from their mean values. For the subsequent discussion they are assumed to be constant.

The reaction coordinate, projected on the NCO plane, can be followed from the three sets of points A–F shown in Figure 1b. As the nucleophile approaches the carbonyl C atom, the two alkyl substituents R and R′ bend away and the C–O distance becomes slightly longer. The virtual constancy of α shows that the nucleophile approaches along a line. This line is not perpendicular to the C–O bond but forms an angle of about 107° with it. We find approximately the same value of α from parallel studies with other nucleophiles[11] Although we cannot observe the direction of the lone-pair orbital on the nitrogen atom it can safely be assumed to lie close to the local threefold axis of the tertiary amino group. From the experimental data, this direction coincides with the N···C direction within a few degrees, except in the case of methadone where the distance is largest and the angle is about 21°. From this we conclude that there is a strongly preferred orientation for nucleophilic attack, as has been postulated from analysis of kinetic data.[12]

As the RR′C═O system becomes nonplanar the π and π^* orbitals of the carbonyl group develop into a lone-pair orbital on oxygen and an empty sp^n-type orbital on carbon. The closer the approach of the nucleophile, the larger the nonplanarity of the RR′C═O system, the higher the s character of the empty orbital,

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(3) All recent work on transannular N···C═O interactions owes much to the early investigations of Sir Robert Robinson and N. J. Leonard. For an account of the early chemical and spectroscopic studies in this field see N. J. Leonard, *Rec. Chem. Progr.*, **17**, 243 (1956), and references cited therein.

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(9) L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. **18** (1965).

(10) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1963, p 246.

(11) H. B. Bürgi, J. D. Dunitz, and E. Shefter, unpublished results.

(12) D. R. Storm and D. E. Koshland, Jr., *J. Amer. Chem. Soc.*, **94**, 5805, 5815 (1972).

the lower its orbital energy, and the greater its interaction with the nitrogen lone pair. In the initial stages, where the reaction coordinate is not controlled by orbital overlap considerations, the main interaction would appear to be between the local electric dipoles of the nucleophilic and the carbonyl groups. These conclusions are somewhat analogous to the interplay of charge polarization and orbital overlap occurring in the course of SN-type reactions, according to recent SCF–MO calculations.[13]

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(13) J. P. Lowe, *J. Amer. Chem. Soc.*, **93**, 301 (1971).

(14) G. A. Pfeiffer Fellow (1972–1973) of the American Foundation for Pharmaceutical Education; on leave from the School of Pharmacy, State University of New York at Buffalo.

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Low-Lying π-Electron States of *trans*-Butadiene

Sir:

A series of extensive configuration interaction calculations on the π-electron states of *trans*-butadiene has been carried out and will be described in detail elsewhere.[1] They were based on a self-consistent field representation of the σ core, obtained from an all-electron SCF calculation on the ground state using a double-ζ contracted Gaussian basis set[2] (the SCF energy was -154.87712 hartree). In line with recent calculations on ethylene[3–5] in which the singlet $(\pi\pi^*)$ state was found to have a diffuse charge distribution,[6] the π basis was augmented with two diffuse $2p\pi$ functions (Gaussian exponents 0.03477 and 0.01075) on each carbon atom. All the configurations which could be constructed by distributing the four π electrons in all possible ways between the 16 SCF occupied and virtual π orbitals (2752 configurations for ^1A_g, 3556 for ^3A_g, 924 for ^5A_g, 2688 for ^1B_u, and 3584 for ^3B_u) were included in the configuration interaction treatment, which can thus be characterized as full π-electron CI with a frozen SCF σ core.

The main results are summarized in Table I in terms of the vertical excitation energies from the ground state (the computed ground state CI energy was -154.94015 hartree). The electronic states are characterized as either valence-like or diffuse (Rydberg-like), in terms of the spatial extent of the wave function; no intermediate cases have been found.[1]

Table I. Calculated and Experimental Vertical Excitation Energies for Selected π-Electron States of *trans*-Butadiene (in eV)

State	Excitation energies		
	Calcd	Optical	Electron impact[a]
	Valence Single-Excitation States		
1^3B_u	3.45	3.22[b]	3.20
1^3A_g	5.04	(3.90[b])	4.91
	Valence Double-Excitation States		
2^1A_g	6.77		
3^3B_u[c]	8.08		
1^5A_g	9.61		
	Diffuse (Single-Excitation) States[d]		
1^1B_u	7.05	6.05[e]	5.92
2^1B_u	8.06	$\gtrsim$7.06[e]	7.28
3^1A_g	7.82		
4^1A_g	7.87		

[a] Reference 7. [b] D. F. Evans, *J. Chem. Soc.*, 1735 (1960); the 3.9 eV state has not been confirmed by other data and is considered spurious. [c] The 2^3B_u state is a Rydberg state and has a calculated excitation energy of 7.14 eV. [d] The calculated excitation energies for the diffuse states are believed too high by about 1 eV, see text. [e] W. C. Price and A. D. Walsh, *Proc. Roy. Soc., Ser. A*, **174**, 220 (1940). The 7.05 eV state was assigned by R. S. Mulliken, *J. Chem. Phys.*, **7**, 121, 373 (1939), as ^1A_g.

The two lowest triplet states, 1^3B_u and 1^3A_g, are found to be valence states with calculated vertical excitation energies of 3.45 and 5.04 eV, respectively, in good agreement with recent electron impact[7,8] and ion impact[9] spectra. Agreement is less good for the corresponding singlet states. In contrast to the assumptions of π-electron theory and in line with the *ab initio* results for planar ethylene,[3–5] the $1,2^1B_u$ and $3,4^1A_g$ states of butadiene are found to be Rydberg-like in character (the 2^1A_g state is of a different type and is discussed further below). While the σ core obtained from the ground-state SCF calculation appears to be adequate for the treatment of the low-lying valence states,[3] such as 1^3B_u and 1^3A_g, it is less appropriate for the diffuse Rydberg-like states; thus, in ethylene,[3] relaxation of the σ core for the singlet $(\pi\pi^*)$ state (upon carrying out an SCF calculation for the excited state) lowered the computed excitation energy by 0.6 eV (but this effect was smaller in recent CI calculations on butadiene with a smaller basis set by Shih, Buenker, and Peyerimhoff[10]). Furthermore, σ orbital correlation (neglected here and by Shih, *et al.*) appears to affect the $\pi\pi^*$ singlet states more than the ground state.[4,11] The calculated vertical excitation energies are therefore expected to be too high, as indeed appears to be the case. The assignments used for these states[1] in Table I were suggested independently by Shih, *et al.*[10]

In addition to the states discussed above, three states with valence-like charge distributions were found with vertical excitation energies of 6.67 (2^1A_g), 8.08 (3^3B_u), and 9.61 eV (1^5A_g). They could not be correlated with any spectroscopic states and were found to be predominantly double-excitations relative to the ground-state Hartree–

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(6) It should be noted that the diffuse nature of the $(\pi\pi^*)$ singlet state of planar ethylene has been questioned by a number of workers, notably H. Basch and V. McKoy, *J. Chem. Phys.*, **53**, 1628 (1970), and J. A. Ryan and J. L. Whitten, *Chem. Phys. Lett.*, **15**, 119 (1972), but the results of the recent CI calculations of Bender, *et al.*,[4] and of H. Basch, *Chem. Phys. Lett.*, **19**, 323 (1973), while indicating that electron correlation has a significant effect on the charge distribution in this state, do not support the objections of these authors.

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(9) J. H. Moore, Jr., *J. Phys. Chem.*, **76**, 1130 (1972).

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