efficient of the product of the bathochromic shift. This value was obtained indirectly by simultaneous solution of the rate equation at $t = 70$ and 140 sec to give a value of 1.247. The rate constant was obtained as the slope of log $[1/(1.247 - A_{308.5})]$ vs. t, which varied linearly from $t = 40$ to $t = 150$ sec. The rates of both hypsochromic shifts were too fast to be measured. Although the rate of the 5-mμ bathochromic shift was slow, its rate constant was not obtained. The ratios[6] of the molar extinction coefficients at λ_{max} were approximately 22 for $A_{308.5}/A_{280}$ and 13 for A_{275}/A_{280}.

Solutions of 1 in 0.037 M potassium phosphate (pH 7.38) showed a plain positive rotatory dispersion curve and were transparent to circularly polarized light above 220 mμ. Rotatory dispersion spectra of mixtures of isomerase and 1 showed a negative Cotton effect with a trough at 298 mμ and a peak at 255 mμ. The Cotton effect had inverted sign at 280 mμ. The same solution showed a negative dichroic absorption band with a wavelength of maximum dichroic absorption at 280 mμ. The position of the Cotton effect was not affected by those conditions which led to the spectral shifts in the absorption spectrum of the isomerase-generated chromophore, although the amplitude of the Cotton effect was decreased. Dialysis of isomerase against 1 showed that both the Cotton effect and the dichroic absorption band were associated only with solution containing isomerase, 1, and the absorption chromophore (the retentate). The isomerase-generated chromophore could be detected in the diffusate, but the diffusate showed only a plain positive rotatory dispersion curve and no dichroic absorption.

The reversible NaOH-induced bathochromic shift of 28.5 mμ in the absorption spectrum of the isomerase-generated chromophore suggests that it is a weak acid. The first-order rate constant of 1.9×10^{-3} sec^{-1} is of the same order of magnitude as many carbon acids.[7] The two hypsochromic shifts of 28.5 and 33.5 mμ in the absorption spectrum of the conjugate base of the isomerase-generated chromophore lead to the conclusion that the acid can exist in two tautomeric forms. Since the Cotton effect and the dichroic absorption band do not undergo pH-dependent shifts, whereas the absorption spectrum does, it can be concluded that the absorption chromophore is either optically inactive or that its asymmetry is destroyed by production of its conjugate base. The dialysis experiment indicates that the isomerase-generated chromophore is optically inactive, however, and it appears that the Cotton effect and dichroic absorption band are due either to the association of the absorption chromophore with isomerase or the production of the aldehydo form of 1 (3).

The scheme shown in Figure 1 interprets these results in terms of the absorption chromophore produced from 1 by isomerase as being a β-diketone phosphate 5. The three ultraviolet absorption chromophores with λ_{max} 275, 280, and 308.5 mμ then correspond to the β-hydroxy enone 6, the β-diketone 5, and the enolate anion 4, respectively. The spectral shifts observed for the isomerase-generated chromophore are close to those observed for 2,4-pentanedione, as are the ratios of
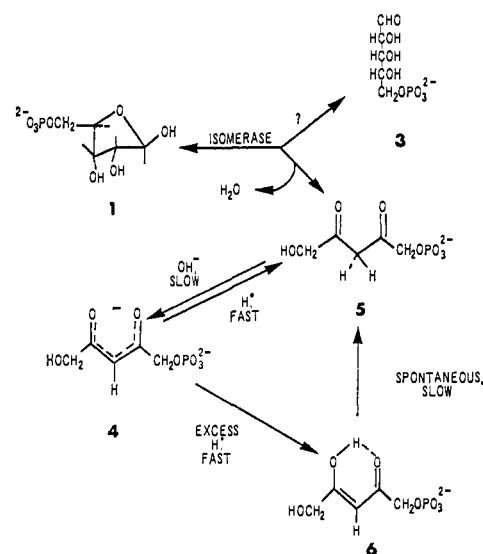
(6) We have been unable to assign a molar extinction coefficient to the isomerase-generated chromophore. An ϵ of approximately 800 is indicated from the colorimetric assay, however.
(7) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 10.

Figure 1. Scheme which proposes the structures associated with the spectral displays of the product of the isomerase-catalyzed transformation of 1.

molar extinction coefficients at λ_{max}.[8] Furthermore, the preferred tautomeric form of β-diketones in polar solutions is known to be the diketo form.[8] The first-order rate constant for the production of 4 from 5 is less than that of 2,4-pentanedione (1.7×10^{-2} sec^{-1}),[7] but the phosphate group in the 5 position would be expected to lower the rate constant by repelling the approach of hydroxide ions to the methylene hydrogens in the 3 position.

The β-diketone phosphate 5 differs from 2 by the elements of water. The rehydration of 5 to generate 2 could be accomplished by another enzyme, although no such enzyme was detected. The possibility that 2 is also generated from 1 by isomerase exists, although the dialysis experiment indicates that this is not the case. The combination of two asymmetric centers and a carbonyl group in 2 should give rise to a dichroic absorption band and a Cotton effect, both of which should be centered in the region from 270 to 290 mμ. If 2 were not stable to dialysis or if the molecular ellipticity of 2 was very low, then it would not have been detected.

(8) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, pp 69 and 267.

F. C. Knowles, N. G. Pon
Department of Biochemistry, University of California
Riverside, California 92502

Concerning the $\sigma_R{}^0$ Scale of Substituent π Delocalization Parameters. Theory and Experiment[1]

Sir:

We report herein accord between the empirical $\sigma_R{}^0$ scale of substituent π delocalization power[2] and a theoretically calculated scale of such effects. The latter scale has been obtained by use of Pople's CNDO/2 theory.[3] The comparison is timely both with regard

(1) This work was supported in part by the National Science Foundation.
(2) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Amer. Chem. Soc.*, 81, 535 (1959).

Table I. Theoretical and Empirical Scales of Substituent π Delocalization Parameters

Subst X	$10^4 \Sigma \Delta q_{(\pi)}$	$10^4 \Delta q^p_{(\pi)}$	$10^4 \Sigma \Delta q_{(tot)}$	μ_{calcd}	$\mu_{obsd}{}^a$	$\sigma_R{}^{0\ b}$	$\sigma_{(p)}{}^{0\ b}$
$N(CH_3)_2{}^c$	-798.0	-468.0	$+362.0$	1.15	1.61	-0.52	-0.47
OH	-663.0	-425.0	$+1003.0$	1.72	1.41	-0.42	-0.15
F	-489.0	-271.0	$+1964.0$	1.62	1.60	-0.34	$+0.17$
CH_3	-125.0	-151.0	-15.0	0.20	0.37	-0.10	-0.15
H	0.0	0.0	0.0	0.0	0.0	0.00	0.00
CF_3	$+134.0$	$+244.0$	$+571.0$	2.59	2.87	$+0.13$	$+0.54$
CN	$+170.0$	$+75.0$	$+778.0$	3.23	4.2	$+0.14$	$+0.66$
NO_2	$+201.0$	$+349.0$	$+1858.0$	4.94	4.28	$+0.19$	$+0.83$
CHO	$+391.0$	$+206.0$	$+343.0$	2.52	$(2.8)^d$	$+0.26^e$	$+0.58$

[a] Gas phase values taken from A. L. McClellan "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963. [b] Taken from ref 2 and P. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968). [c] Calculations based upon structural data reported by L. V. Vilkov and T. P. Timasheva, *Dokl. Akad. Nauk SSSR*, **161** (2), 351 (1965); *Chem. Abstr.*, **63**, 2531 (1965). [d] Benzene solution. [e] Calculated from results of ref 9a and R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, **90**, 1757 (1968).

to current questions regarding the empirical scale[2,4] and the utility of the CNDO/2 theory for calculation of molecular properties which depend critically upon the electronic distribution.
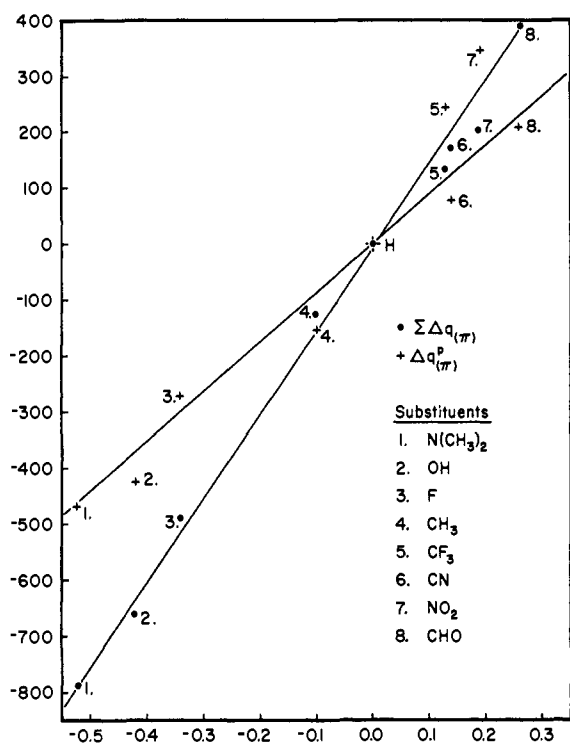

Figure 1. Relationship between theoretical and empirical substituent parameters for π electron delocalization: ordinate, $\Sigma \Delta q_{(\pi)}$ or $\Delta q^p_{(\pi)}$ as indicated by $\bullet$ or $+$, respectively; abscissa, $\sigma^0{}_R$. Line slopes are: $\Sigma \Delta q_{(\pi)}$, $0.15e/\sigma^0{}_R$ and $\Delta q^p_{(\pi)}$, $0.10e/\sigma^0{}_R$.

We believe the most reliable theoretical scale is obtained from the quantity $\Sigma \Delta q_{(\pi)}$, where $\Delta q_{(\pi)}$ is the excess π charge density at ring carbon and the summation is taken over all six carbon atoms of a monosubstituted benzene XC_6H_5. The selection of $\Sigma \Delta q_{(\pi)}$ is based upon its relatively large magnitude (as compared with $\Delta q_{(\pi)}$ at a single ring position) and the fact that effects of sub-

stituent polarization without π charge transfer[5] on individual ring positions should largely cancel in the summation over the six ring atoms. Further, $\Sigma \Delta q_{(\pi)}$ is a substituent property since it represents a simple basis for obtaining the net π charge transferred by the substituent. In keeping with the empirical scale, this quantity is zero for the conventional H atom substituent.

In Table I are given values of $\Sigma \Delta q_{(\pi)}$ obtained by CNDO/2 calculations for a critical selection of common substituent groups. The calculations were carried out to a self-consistency in charge densities[6] of $\pm 5 \times 10^{-4}$ using the best values of structural parameters[7] (interatomic distances and bond angles) available for each individual molecule. For comparison, Table I also gives values of $\Delta q^p_{(\pi)}$, the excess π charge density at the *para* position, and $\Sigma \Delta q_{(tot)}$ relative to H, where $\Sigma \Delta q_{(tot)}$ is the summed excess total charge density (σ and π) on ring carbons and hydrogens. This quantity gives the scale of the total charge transferred by the substituent. The calculated and experimental (gas phase) dipole moments are listed for each molecule. The previously reported[3] general character of good agreement in these quantities is to be noted. Finally, Table I lists $\sigma_R{}^0$ values together with the experimental σ^0 values from which the former were derived[2] ($\sigma_R{}^0 \equiv \sigma^0 - \sigma_I$).

Figure 1 shows a plot of $\Sigma \Delta q_{(\pi)}$ values vs. $\sigma_R{}^0$ values. The excellent linear correlation (RMS $= 443$, SD $= 34.5$) shown in Figure 1 provides important mutual support for the approximations involved in both the theoretical and empirical treatments.[8] This conclusion is made more critical by the fact that the scales of substituent effects provided by such composite quantities as $\Sigma \Delta q_{(tot)}$, μ, or σ^0 bear no such close correspondences to one another or to that for the separated π delocalization effects (cf. Table I). It is of interest that both the theoretical and empirical results support the conclusion that the "classically saturated" substituents CH_3 and CF_3 behave in the ground state as pseudo-unsaturated

(3) (a) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967), and earlier references given therein; (b) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

(4) (a) O. Exner, *Collect. Czech. Chem. Commun.*, **31**, 65 (1966); (b) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jap.*, **39**, 2274 (1966); (c) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(5) Cf. J. N. Murrell "Theory of Electronic Spectra of Organic Molecules," Methuen and Co. Ltd, London, 1963, Chapter 10.

(6) Program 91 of G. A. Segal supplied by Quantum Chemistry Program Exchange was modified to accomplish this objective.

(7) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965.

(8) The SD of fit is 6–7% of RMS using either $\sigma_R{}^0$ or σ_R (the latter is obtained from reactivities of benzoic acids and derivatives, $\sigma_{(p)} - \sigma_I \equiv \sigma_R$). However, for the other resonance-effect scales given in ref 4 the SD is 17–25% of RMS.

groups, the former being a net π donor ($-$R) and the latter a net π acceptor ($+$R) substituent.

The precision of the correlation of $\Sigma\Delta q_{(\pi)}$ vs. σ_R^0 is suggestive of a similar correlation[9] of $\Delta q^p_{(\pi)}$ vs. σ_R^0. The CNDO/2 calculations give somewhat less satisfactory results in that a plot of the excess π charge density at the para carbon atom, $\Delta q^p_{(\pi)}$, vs. σ_R^0 is less precise (RMS = 301; SD = 80; cf. Figure 1). However, the relationship $\Delta q^p_{(\pi)} \simeq 0.7 \, (\Sigma\Delta q_{(\pi)})$, is generally a useful approximation of the calculated results. Further, the slope of $\Delta q^p_{(\pi)}$ vs. σ_R^0 (Figure 1) of $0.10e/\sigma_R^0$ is of the same order of magnitude as estimated from interpretations of nmr shifts.[9] Since the calculated absolute values of $\Delta q^p_{(\pi)}$ are actually greater than $\Sigma\Delta q_{(\pi)}$ for the substituents CH_3, CF_3, and NO_2 (Table I) some small deficiencies of the theory are suggested. Additional features of these calculations as well as those for meta- and para-substituted fluorobenzenes will be discussed in a subsequent full paper.

Acknowledgment. We are pleased to acknowledge the assistance of Dr. Stanton Ehrenson in the indicated modification of Program 91.

(9) (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen and G. T. Davis, J. Amer. Chem. Soc., 85, 3146 (1963); (b) G. E. Macie and J. J. Natterstad, J. Chem. Phys., 42, 2427 (1965); (c) P. C. Lauterbur, Tetrahedron Lett., 8, 274 (1961); (d) H. Spiesecke and W. G. Schneider, J. Chem. Phys., 35, 731 (1961); (e) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, J. Amer. Chem. Soc., 82, 5846 (1960).

R. T. C. Brownlee, R. W. Taft

Department of Chemistry, University of California, Irvine
Irvine, California 92664

The Base Hydrolysis of trans-[Co(NH₃)₄¹⁵NH₃Cl](ClO₄)₂ in the Presence of Azide Ion

Sir:

We wish to correct an error reported in a previous communication[1] on the base hydrolysis of trans-[Co-(NH₃)₄¹⁵NH₃X]²⁺ ions (where X = Cl, Br, NO₃). In one experiment where trans-[Co(NH₃)₄¹⁵NH₃Cl]-(ClO₄)₂ was treated with NaOH ($\sim$0.1 M) in the presence of N₃⁻ ion ($\sim$4 M) it was reported that the hydroxo product showed approximately 40% rearrangement to the cis form while the [Co(NH₃)₅N₃]²⁺ product was 100% trans.

The validity of this result has recently been questioned,[2] and we find by repeating the experiment more carefully as previously described that 60% of the product chloride was unreacted chloro complex and that the pmr spectrum originally given was due substantially to the chloro perchlorate. The hydrolysis has now been repeated more carefully with a slightly larger sample of the enriched complex over a longer period. The 100-Mc pmr spectra of the reactant, trans-[Co(NH₃)₄¹⁵NH₃Cl](ClO₄)₂, and the isolated aquo complex in DMSO are given in Figure 1 (a and b). The spectrum of the aquo complex is essentially unchanged from that found previously[1] and indicates $\sim$40% rearrangement from trans to cis. However, the pmr

(1) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, J. Am. Chem. Soc., 89, 5129 (1967).

(2) We are grateful to Professor F. Nordmeyer for activating our suspicions over this aspect of the original publication.
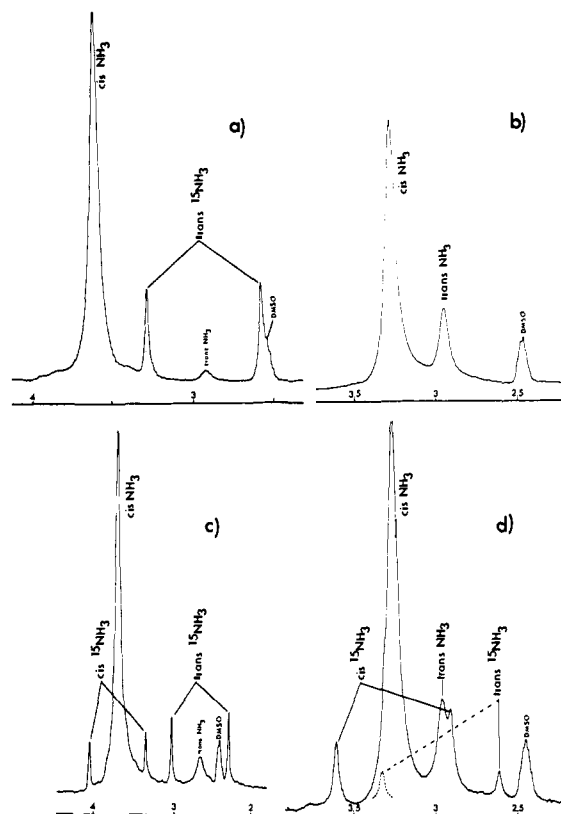
Figure 1. Pmr spectra (100 Mc, scale ppm) for (a) trans-[Co(NH₃)₄-¹⁵NH₃Cl](ClO₄)₂, (b) [Co(NH₃)₅N₃](ClO₄)₂, (c) cis- and trans-[Co(NH₃)₄¹⁵NH₃OH₂](ClO₄)₃ reaction product, (d) cis- and trans-[Co(NH₃)₄¹⁵NH₃N₃](ClO₄)₂ reaction product in dimethyl-d_6 sulfoxide containing a trace of D_2SO_4 (98%).

spectrum of the isolated azido complex (ϵ_{max} 270) is substantially different from that recorded previously.

Figure 1 (c and d) shows the 100-Mc pmr spectra of the isolated azido complex compared with that for the unenriched [Co(NH₃)₅N₃](ClO₄)₂ complex in DMSO. The signals can be assigned unequivocally by using the 70-cps coupling constant between the ¹⁵NH₃ proton doublet and the symmetry relationship between these signals and those due to the related broad ¹⁴NH₃ protons. Approximately 70% rearrangement is indicated, and this result is more in keeping with that for the hydroxo product and with the results obtained for base hydrolysis of cis- and trans-[Co(en)₂NH₃X]²⁺ ions (X = Cl, Br, NO₃) in the presence of N₃⁻.[3]

The new result does not alter the conclusions reached in the previous article[1] except that it is no longer required that N₃⁻ react with the proposed five-coordinate intermediate in a stereospecific manner. In fact, if a trigonal-bipyramidal intermediate obtains, then the stereochemistry of the competition result can be accommodated by an approximately statistical addition of N₃⁻ to the edges of the trigonal plane, provided the ¹⁵N label remains in the trigonal plane.

trans-[Co(NH₃)₄(¹⁵NH₃)Cl](ClO₄)₂ was prepared as described earlier.[1] The complex (1.1 g) was dissolved in 15 ml of dilute HClO₄ (10^{-3} M) and added to a solution of NaOH (50 ml, 0.2 N) saturated with NaN₃ at 25°. After 30 min the solution was cooled in an ice bath and excess LiCl was added to precipitate the formed

(3) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, J. Am. Chem. Soc., in press.