J. Am. Chem. Soc. 1988, 110, 5511-5517

Detection of Hyperconjugative Effects in Experimentally Determined Structures of Neutral Molecules

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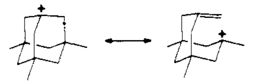
Abstract: In order to find experimental evidence from X-ray, microwave, or electron-diffraction data for hyperconjugation in neutral molecules, the geometry of tetrahedral carbon atoms bonded to electron-poor trigonal centers (positive hyperconjugation) or electron-rich trigonal centers (negative hyperconjugation) has been analyzed with respect to the dependence of bond properties on the torsion angle between the bonds emanating from the tetrahedral center and the "electron-poor" or "electron-rich" orbital at the trigonal center. Ab initio calculations of several conformations of chloroacetaldehyde and of isopropylamine were performed to derive geometry and energy changes during the rotation around the C–C or the C–N bond respectively. The comparison of experimental and theoretical fragment structures for several cases shows similar effects and thus supports the model of hyperconjugation, which was originally derived from the results of MO calculations.

Hyperconjugation belongs to those effects whose existence was questioned for a long time. The term hyperconjugation was introduced by Mulliken[1] nearly half a century ago and first used for the description of the interaction between a multiple bond and a saturated group ("first-order hyperconjugation") or between two saturated groups ("second-order hyperconjugation"). From the very beginning, it was stated that "this is a mild sort of conjugation, apparently not recognized as such hitherto".[1] Only for excited states were appreciable effects expected. In 1958, Mulliken extended the range of application of the concept to alkyl radicals and alkyl cations,[2] and here the calculations predicted drastic effects. Many results from spectroscopic and solvolytic examinations[3] and MO calculations[4] were interpreted according to the resonance formulas presented. Early predictions[5] about the deviations of bond lengths and bond angles from the expected values due to hyperconjugation could be confirmed by few experimental data, although the accuracy of structural parameters was much lower than today. It is the aim of this work to analyze experimental data of several classes of structures of neutral molecules with regard to deviations from an "ideal geometry" (i.e., only steric interactions and conjugation in π systems occurs) that can be explained by hyperconjugation.

Expected Changes of Molecular Geometry

In a recent review article, Radom[6] discussed energetic and structural changes in the calculated structures of a wide variety of both neutral and charged molecules. He analyzed the conformational behavior of β-substituted ethyl cations $XCH_2CH_2^+$. The bond of an electropositive substituent C–X strongly interacts with the empty p-orbital when they stand syn- or antiperiplanar with regard to each other. This results in a weakening of the C–X bond and a strengthening of the C–C bond. The dependence of the hyperconjugative interaction on the torsion angle X–C–C–*p*C (*p*C is a point on the symmetry axis of the empty p orbital) is in accordance with the experimentally determined dependence of NMR coupling constants[7] and isotope effects[8] on the torsion angle. The drastic deviations of the geometry of the 3,5,7-trimethyl-1-adamantyl cation **1** from the geometry of an unpertubed section of the diamond lattice[9] can be easily explained by strong C–C hyperconjugation, as proposed by Olah, Schleyer et al.[10] for several substituted 1-adamantyl cations.



1 1'

To support the interpretation of the bond length deviations, the bond angles of the symmetrized structure of **1** were used to construct orthonormal s–p hybrid orbitals[11] (see Figure 1). The symmetry axes of these orbitals coincide with the straight lines through the bond vectors (trigonal atoms) or deviate as little as possible from them (tetrahedral atoms).[12]

The resulting hybrid orbital compositions are in agreement with an influence of resonance formulas of type **1'** on the structure of **1**. The "empty p orbital" at C1 is of type sp^{22} (i.e., practically a pure p orbital, although the pyramidalization of C1 is 0.21 Å). The orbital on C2 in the direction toward C3 has a similar high p content and gives an overlap integral with the sp^{22} hybrid at C1 ($S = -0.19$), whose absolute value is comparable to that in

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(1) Mulliken, R. S. *J. Chem. Phys.* **1939**, *7*, 339. Mulliken, R. S.; Rieke, C. A.; Brown, W. G. *J. Am. Chem. Soc.* **1941**, *63*, 41.

(2) Muller, N.; Mulliken, R. S. *J. Am. Chem. Soc.* **1958**, *80*, 3489.

(3) Some selected publications: Edlund, U. *Org. Magn. Reson.* **1978**, *11*, 516. Fischer, W.; Grob, C. A. *Helv. Chim. Acta* **1978**, *61*, 1588.

(4) Radom, L. *Aust. J. Chem.* **1974**, *27*, 231. Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061. Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 2* **1985**, 257. Pross, A.; Radom, L.; Riggs, N. V. *J. Am. Chem. Soc.* **1980**, *102*, 2253. Hehre, W. J. *Acc. Chem. Res.* **1975**, *8*, 369, and references cited therein.

(5) *Conference on Hyperconjugation, Indiana University, Bloomington, 2-4 June 1958*; Pergamon: London, 1959; pp 74–117.

(6) Radom, L. *Prog. Theor. Org. Chem.* **1982**, *3*, 1.

(7) Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106.

(8) Siehl, H.-U.; Walter, H. *J. Chem. Soc., Chem. Commun.* **1985**, 76. Saunders, M.; Telkowski, L ; Kates, M. R. *J. Am. Chem. Soc.* **1970**, *99*, 8070. Forsyth, D. A.; Botkin, J. H.; Osterman, V. M. *J. Am. Chem. Soc.* **1984**, *106*, 7663. Botkin, J. H.; Forsyth, D. A.; Sardella, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 2797. Sunko, D. E.; Hehre, W. J. *Prog. Phys. Org. Chem.* **1983**, *14*, 205, and references cited therein.

(9) Laube, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 349.

(10) Olah, G. A.; Prakash, G. K. S.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1985**, *107*, 2764.

(11) (a) Trigonal atoms: Haddon, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 2837. (b) Tetrahedral atoms: Laube, T. *J. Comput. Chem.*, in press.

(12) The procedures for the construction of these orbitals do not require SCF-MO calculations on the molecules, and therefore, they can be applied to a large number of molecules.[13] Because these methods use only the information from the bond angles,[14] a careful selection of the examples is needed in order to exclude molecules with large angle strain or steric strain (i.e., open-chain or six-membered ring compounds were preferred).

(13) All other localization procedures require the calculation of SCF-MO wave functions: Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457. Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300.

(14) Another method to analyze the information contained in the bond angles at a tetrahedral center is the use of symmetry coordinates: Murray-Rust, P.; Bürgi, H.-B.; Dunitz, J. D. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **1979**, *A35*, 703. Luef, W.; Keese, R.; Bürgi, H.-B. *Helv. Chim. Acta* **1987**, *70*, 534.

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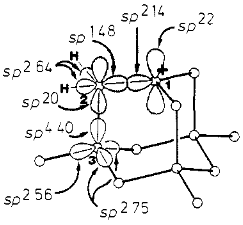
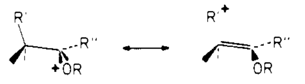


Figure 1. Orthonormal s–p hybrid atomic orbitals of the carbon atoms 1–3 of the symmetrized (C_{3v}) structure of the 3,5,7-trimethyl-1-adamantyl cation **1**.[9] The C–H bond vectors at C2 were included with smaller weights than the C–C bond vectors. The partial C1–C2 π bond is indicated by raster. Bond lengths: C1–C2 = 1.44 Å, C2–C3 = 1.62 Å.

normal C–C π bonds ($S \approx 0.27$).[15] The carbon hybrid orbital compositions in the C2–H bonds[16] agree practically with those calculated from the NMR data of Olah et al.[10] The adjusted orbitals for C3 indicate the slight flattening by an increased p content of that hybrid orbital of C3 that is directed toward C2. The σ bond C2–C3 is thus formed by less overlapping hybrid orbitals (S = 0.52) than normal sp^3–sp^3 σ bonds ($S \approx 0.65$). Similar but smaller bond length changes were observed in the crystal structures of O-alkylated[17] or O-metal-complexed ketones[18] **2**.



2 **2'**

Analysis of the Experimental Data

In order to test the validity of the concept of hyperconjugation in neutral ground-state molecules, we have analyzed structural data of several types of α-substituted ketones, amines, and some allyl and benzyl compounds and compared them in several cases with results from ab initio calculations. The Cambridge Crystallographic Database[19] offers nowadays enough data of sufficient accuracy to analyze structures with regard to small geometric changes from expected values due to stereoelectronic effects. The low precision of hydrogen positions in X-ray measurements defeats any analysis that requires their experimentally determined positions. Therefore, the bond direction vectors toward hydrogen atoms at tetrahedral carbon atoms with three well-defined substituents were calculated with the POAV2 method.[11a] The hybrid orbital composition of the carbon atom in a C–H bond is therefore less reliable,[20] because just the considered C–H bond supplies no information itself.

Ketones. Allinger et al.[21] have carried out many ab initio calculations on small molecules that should exhibit hyperconjugative effects. In accordance with the structural parameters found in the crystal structure of **1**, the C$_\alpha$–H bonds in the calculated structures of aldehydes RH$_2$C$_\alpha$–CHO are lengthened and the carbon p character is raised if they are coplanar with the symmetry axis of the p orbital of the carbonyl C atom. The analogous behavior is found for the C$_\alpha$–C$_\beta$ bond in propionaldehyde. The analysis of the carbon hybrid orbital compositions of C–H bonds in the experimentally determined structures of α-branched ketones[22,23] (see Figure 2) shows qualitatively the same behavior. Despite the considerable scattering of the data, the carbon p character is higher when the C–H bond is coplanar with the carbonyl C p orbital. This may be regarded as the structural expression of the higher kinetic acidity if compared to those conformations where the C–H bond lies in the carbonyl plane[24] (**3''**, R = H). It should be emphasized here that we consider a significant cos 2ω component (ω = torsion angle X—C—C=Y) in the adjusted regression functions $\hat{Y}$ as sufficient for the detection of hyperconjugation.

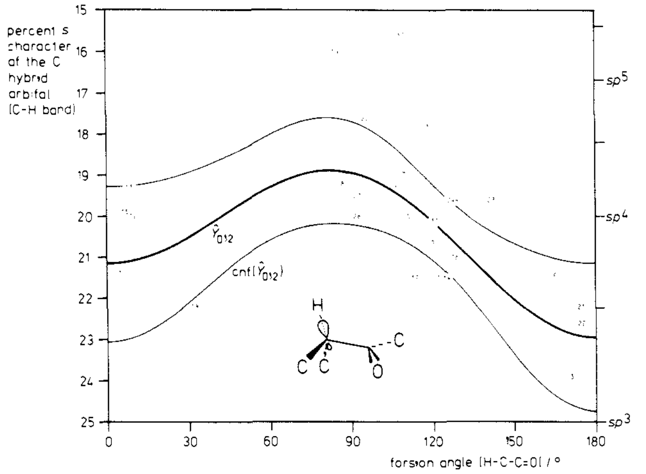
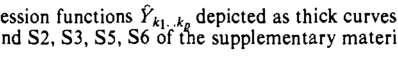


Figure 2. Carbon hybrid orbital composition[11a] of the C—H bonds of α-branched ketones (X-ray data) plotted versus the absolute value of the torsion angle H—C—C=O/deg. The C$_\alpha$—H bond vectors were calculated[11a] from the three well-determined C$_\alpha$—C bond vectors. The data are represented by their item numbers (see Table S3 in the supplementary material). The cos ω term is not significant but large (individual 99% confidence interval[22] for $\hat{\beta}_1$, −0.9 ± 1.3 % s).



3 **3'** **3''**

Figure 3 shows that the C$_\alpha$–C$_\beta$ bond lengths (upper diagram) exhibit a strong scattering (only a significant cos ω component is detectable). The hybrid orbital compositions (lower diagram) scatter less,[20] and the regression function contains significant cos ω and cos 2ω terms.

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(15) Overlap integrals are calculated with the formulas given in: Preuss, H. *Integraltafeln zur Quantenchemie, 1*; Springer-Verlag: Berlin, 1956; p 22.

(16) The hybrid orbital compositions at C2 are less reliable than those at C1 and C3, because the hydrogen atoms at C2 are less precisely determined than the other bond partners.

(17) Montgomery, L. K.; Grendze, M. P.; Huffmann, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749.

(18) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876.

(19) In most cases the structures included in our analysis have $R \leq 0.08$, $\bar{\sigma}_{C-C} \leq 0.01$ Å, no disorder. Cambridge Crystallographic Database: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146.

(20) It should be noted here that thermal motion affects the bond lengths more strongly than the bond angles.

(21) Allinger, N. L.; Schäfer, L.; Siam, K.; Klimkowski, V. J.; Van Alsenoy, C. *J. Comput. Chem.* **1985**, *6*, 331.

(22) All regression functions $\hat{Y}_{k1\ldots kp}$ depicted as thick curves in Figures 2, 3, 5, 7, and 8 (and S2, S3, S5, S6 of the supplementary material) are trigonometric series

$$\hat{Y}_{k1\ldots kp} = \sum_{j=1}^{p} \hat{\beta}_{k_j} \cos(k_j\omega) \equiv \hat{\beta}\cdot\mathbf{X}_0$$

and have been adjusted by least-squares methods on the data points (unit weights). The type of the adjusted functions is arbitrary, e.g. polynomials in ω could be used as well, but the first derivative should be zero at ω = 0° and at ω = 180° because of the periodicity of an even function, i.e. we assume that the sine terms in $\hat{Y}$ needed for the description of individual molecules without a mirror plane at ω = 0° or at ω = 180° are averaged out and raise only the variance. All confidence intervals cnf($\hat{Y}$) are 99% intervals for the true mean value of Y at $\mathbf{X}_0$ and were computed according to $\hat{Y} \pm t_{\nu;0.995}s(\mathbf{X}_0{}^{\mathrm{T}}\mathbf{C}\mathbf{X}_0)^{0.5}$ (ν = number of data points − number of parameters p; $\mathbf{C} = (\mathbf{X}^{\mathrm{T}}\mathbf{X})^{-1}$ and $\hat{\beta} = \mathbf{C}\mathbf{X}^{\mathrm{T}}\mathbf{Y}$; s^2 = estimator of the variance; t = integration limit of the t distribution; see e.g.: Draper, N. R.; Smith, H. *Applied Regression Analysis*; Wiley: New York, 1981; p 94, or textbooks on statistics). Only the significant terms (99%) were included in the regression functions. Bounds for the individual 99% confidence intervals (t distribution) of the regression coefficients $\hat{\beta}_2$ are as follows: Figure 2, 1.6 ± 1.0 % s; Figure 3 (bottom) 1.9 ± 1.8 % s; Figure 5 (top) (2.0 ± 1.0)·10^{-3} Å, (bottom) 1.3 ± 0.3 % s; Figure 7 (top) (−1.4 ± 0.7)·10^{-2} Å for p = 2 and (−1.4 ± 1.3)·10^{-2} Å for p = 3, (bottom) 3.0 ± 1.5 % s; Figure 8 (top) (−8.0 ± 1.3)·10^{-3} Å, (bottom) 2.9 ± 0.7 % s.

(23) In addition to those constraints mentioned in footnote 12, only those bonds were included that interact only with *one* π system, for example a carbonyl group, because the simultaneous interaction with several π systems requires a factorization of the observed effects.

(24) This stereoelectronic effect was first mentioned in: Corey, E. J. *J. Am. Chem. Soc.* **1954**, *76*, 175.

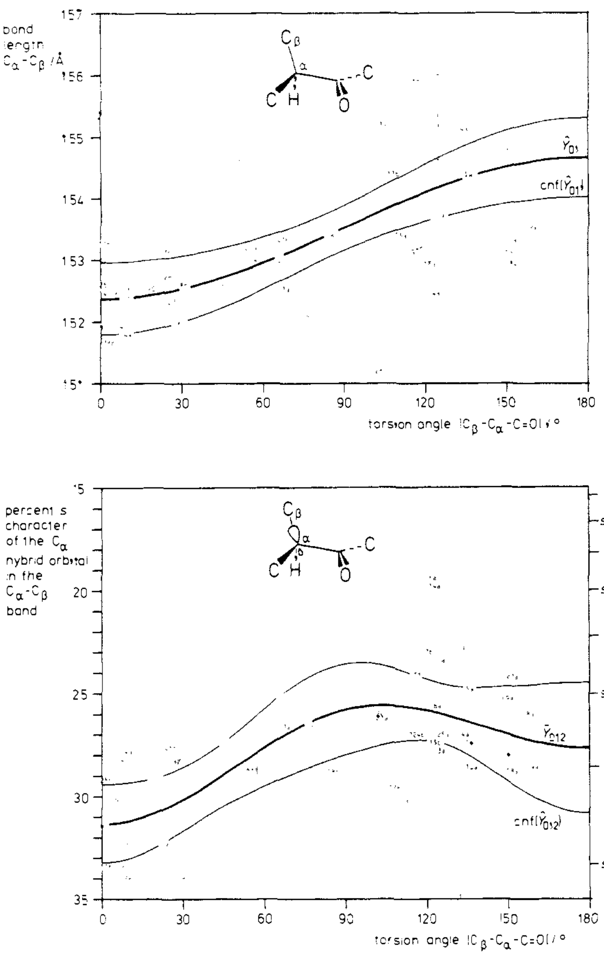
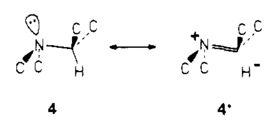


Figure 3. Bond lengths (upper diagram) and C_α hybrid orbital compositions[11a] (lower diagram) of the C_α—C_β bonds of α-branched ketones (X-ray data) plotted versus the absolute value of the torsion angle C_β—C_α—C=O/deg. The numbers refer to the same molecular fragments as in Figure 2; the characters a and b denote the two different C_β atoms (see Table S3 in the supplementary material).

The hyperconjugative interaction of a σ bond with a carbonyl group may be approximately classified as a stabilizing two-center–two-electron interaction [i.e., $\sigma_{C-C}-\pi_{C=O}^* \approx \sigma_{C-C}-p_{C(=O)}$], and this explains the tendency of such a system to raise the overlap between the filled σ-bond orbital and the "empty" p orbital at the carbonyl carbon atom.[25]

Amines. In order to test the validity of the interpretation of the ketone data, we have also analyzed the geometry of tertiary amines (**4**; the designated C atoms are tetrahedral) with one (or more) secondary alkyl substituent(s) (see Figure 4), because these molecular fragments should exhibit a destabilizing two-center–four-electron interaction (σ_{C-H}–n_N) between the C–H bond and the N lone pair if both are coplanar, and this should result in a *lowering* of both p characters, which implies a reduced overlap. Such a behavior has been detected by Egli and von Philipsborn[26] by analysis of the one-bond $^{13}C_\alpha$–H spin coupling constants in cyclic peptides $R_2NC_\alpha HRCONR_2$, where each C_α–H bond simultaneously interacts with the (π-electron-deficient) carbonyl C atom and the (π-electron-rich) N atom bonded to C_α. On the other hand, there also exists experimental evidence for a stabilizing two-center–two-electron interaction (n_N–σ_{C-H}^*), which can also be classified as an anomeric effect. The Bohlmann bands[27] in IR spectra and the easy cleavage[28] of triaminomethanes into guanidinium ions and hydride ions (trapped by H^+ as H_2) are in agreement with this interpretation (see resonance formula **4'**), and under the assumption that this anomeric effect is dominant, one would expect a *raising* of the p characters of the N lone pair and the C hybrid orbital in the antiperiplanar C–H bond (double bond in **4'**!). In the early phase of the C–H bond cleavage, however, there exists an antibonding (repulsive) interaction between the N lone pair lobe and the lobe of the σ_{C-H}^* orbital around the H atom, which opens the N–C–H angle[29] and thus *lowers* the carbon p character in the C–H bond[30].



4 **4'**

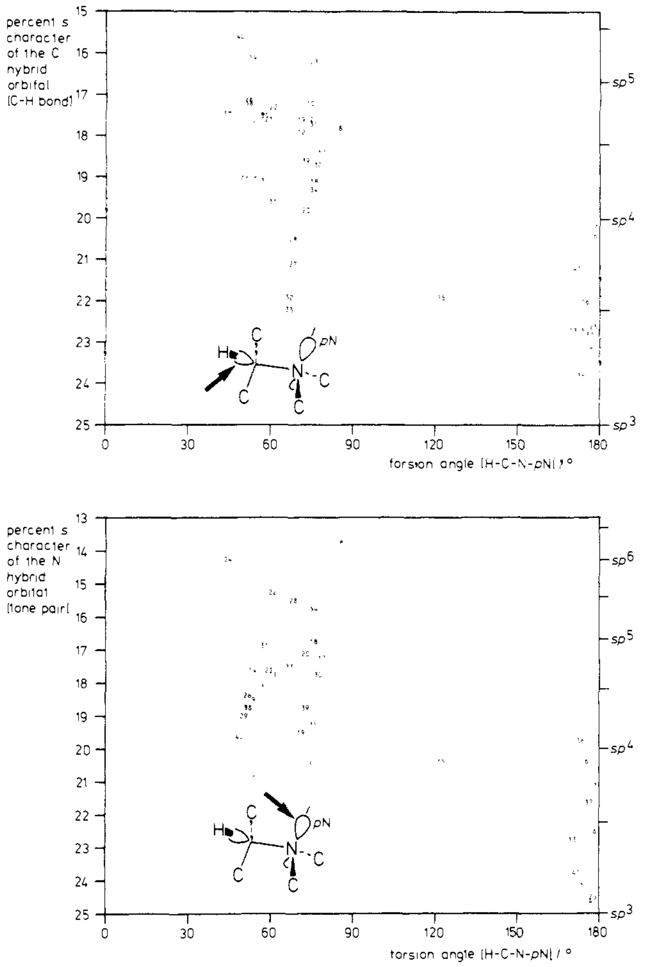


Figure 4. Carbon hybrid orbital composition in the tertiary C–H bond of secondary alkyl groups (upper diagram) and nitrogen lone pair *p*N hybridizations of tertiary amines (X-ray data) plotted versus the absolute value of the torsion angle H–C–N–*p*N/deg. The C–H bond and nitrogen lone pair direction vectors were calculated[11a] from the three well-determined bond vectors at the C or the N atoms respectively. The data are represented by their item numbers (see Table S4 of the supplementary material).

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[25] See also: Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540, and references cited therein.

[26] Egli, H.; von Philipsborn, W. *Helv. Chim. Acta* **1981**, *64*, 976.

[27] Bohlmann, F. *Chem. Ber.* **1958**, *91*, 2157. See also: Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 1189. Profeta, S., Jr.; Allinger, N. L. *J. Am. Chem. Soc.* **1985**, *107*, 1907.

[28] Erhardt, J. M.; Wuest, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 6363. Atkins, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6364.

[29] Reed, A. R.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1987**, *109*, 7362.

[30] In later phases of the cleavage into an iminium ion and a hydride ion the p characters of the N and the C atom should raise again. In the few examples of acetals[31] (cleavage into a ketone and a leaving group) and ester enolates[32] (cleavage into a ketene and a leaving group), where one observes *large* differences between the lengths (up to 0.13 Å) of the two C–O bonds emanating from a C atom, the adjustment of hybrid orbitals on the central C atoms yields, as expected, *high* p characters for the orbitals toward the leaving group [see example **2a** in ref 31 (≡ example **3** in ref 11b), $sp^{5.7}$; for the ester enolates **1**–**3** in ref 32 one finds hybrids of type $sp^{3.3}$, $sp^{3.1}$, and $sp^{2.9}$].

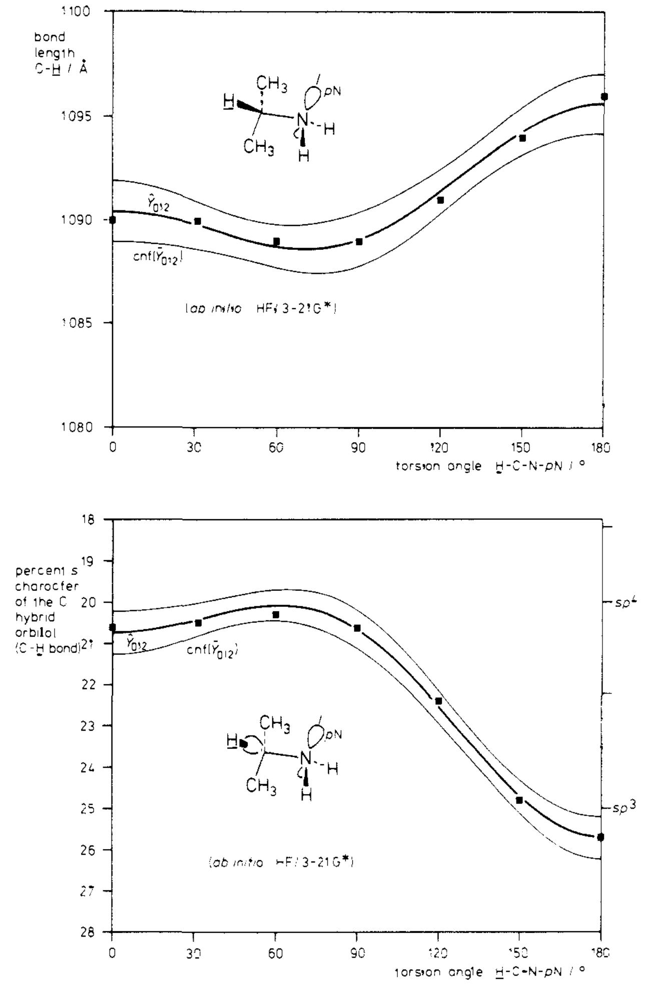

Figure 5. Carbon-hydrogen bond lengths (upper diagram) and C hybrid orbital compositions[11b] of the tertiary C-*H* bond in isopropylamine as functions of the torsion angle *H*-C-N-*p*N/deg. For numerical values, see Tables S5 and S6 of the supplementary material.

The experimental data presented in Figure 4 show indeed a *lower* p character for both orbitals, which become after the cleavage pure p orbitals, if they are in antiperiplanar arrangement ($\omega \approx 180°$); for the examples with a gauche arrangement, the reduced absolute value of the overlap integral between the two hybrid orbitals due to $\omega \approx 60°$ allows higher p characters.[33] In order to analyze the agreement between the data of the experimentally determined structures (Figure 4) and calculated structures, and because the C-H bond lengths are difficult to determine, we have carried out a series of ab initio calculations on isopropylamine, where in each geometry optimization the torsion angle ω was constrained to be a multiple of 30°.

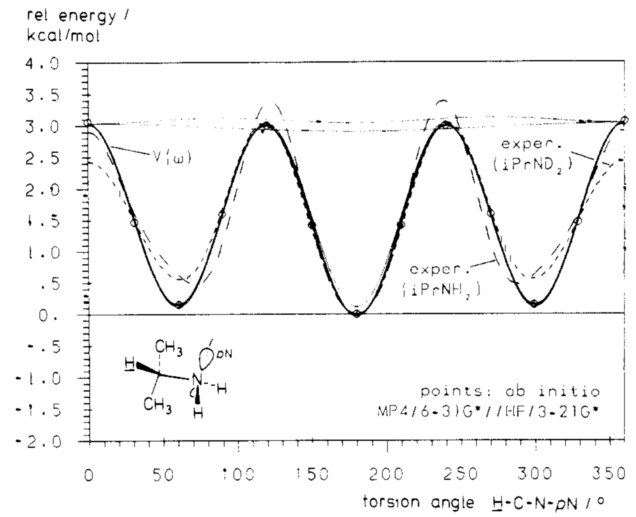

Figure 6. Relative energies of several conformations of isopropylamine (points). The adjusted function $V(\omega)$ (thick curve; the three cos components are vertically shifted and drawn as thin curves) shows a good agreement with the experimentally determined potential energy curves for isopropylamine and its dideuteriated isotopomer[34] (dashed curves) for torsion angles about 180°.

Some selected structural data are shown in Figure 5; the energies are shown in Figure 6. The lengthening of the C-H bond in antiperiplanar arrangement with the N lone pair (Figure 5, upper diagram) is in agreement with the experimentally determined weakening[27] of the bond and can only be explained by an anomeric effect. Nevertheless, the adjustment of hybrid orbital vectors[11b] on the central C atoms shows the decrease of the p character for the anti conformer (H-C-N-pN $\approx 180°$) if compared with the gauche conformer as found in the experimental structures[35] (Figure 4). The widely applied least-squares adjustment of a truncated Fourier series[36] allows a separation of the potential energy $V(\omega)$ into a onefold (dipolar and steric interactions), a twofold (hyperconjugative interactions), and a threefold term (bond electron pair repulsions):

$$V(\omega) = V(0) + \sum_{i=1}^{3} V_i(1 - \cos i\omega)/2$$

The results (Figure 6) show that the onefold and the twofold terms in $V(\omega)$ are very small; this observation can be explained with a neutralization of the stabilizing and destabilizing electronic interactions (both should exhibit the same dependence on the torsion angle). Therefore, the potential energy function $V(\omega)$ is dominated by the threefold term, and this can be regarded as indirect evidence for the destabilizing hyperconjugative $\sigma_{\mathrm{C-H}}$-n_{N} interaction.

α-Chloro Ketones. Corey concluded on the basis of IR and UV data that the axial and the equatorial chlorine atoms in 2-chlorocyclohexanones display different behavior.[37] The same conclusion was drawn by Allinger from dipole moment measurements.[38] The unexpected high amount of the conformer with an axial chlorine atom was explained by resonance formulas of type **3″** (R = Cl), whereas the equatorial C-Cl bond cannot contribute to such a resonance. Another explanation of the conformational behavior of α-halo ketones was based on the in-

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(31) Chadwick, D. J.; Dunitz, J. D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 276.

(32) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403.

(33) The larger scattering of the points in the gauche clusters in Figure 4 is in agreement with the fact that the gradient of the overlap integral is smaller for the gauche examples (see also Figure S7 of the supplementary material).

(34) Durig, J. R.; Guirgis, G. A.; Compton, D. A. C. *J. Phys. Chem.* **1979**, *83*, 1313.

(35) A similar dependence of the C-*C* bond lengths and C hybridizations in the C-*C* bonds on the torsion angles *C*-C-N-*p*N can also be detected in the calculated structures. The analysis of the N lone pair hybridizations in the computed rotamers shows no appreciable effect, because the N atom was constrained to have a local mirror plane in each case. The torsion angle between a dummy atom in that plane representing the N lone pair and the tertiary H atom was constrained to be an integer multiple of 30°. The subsequently adjusted N lone pair hybrid vectors[11a] have a slightly different direction, and therefore, the torsion angles *H*-C-N-*p*N in Figures 5 and 6 are not exact integer multiples of 30°. In another set of calculations without these constraints, the N lone pair hybridization exhibited larger changes upon rotation on the C-N bond with remote similarity to the experimental data in Figure 4, whereas the functions corresponding to those depicted in Figures 5 and 6 were practically identical.

(36) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371.

(37) Corey, E. J. *Experientia* **1953**, *9*, 329. Corey, E. J. *J. Am. Chem. Soc.* **1953**, *75*, 2301. Corey, E. J.; Topie, T. H.; Wozniak, W. A. *J. Am. Chem. Soc.* **1955**, *77*, 5415. Corey, E. J.; Burke, H. J. *J. Am. Chem. Soc.* **1955**, *77*, 5418.

(38) Allinger, N. L.; Allinger, J.; Freiberg, L. A.; Czaja, R. F.; LeBel, N. A. *J. Am. Chem. Soc.* **1960**, *82*, 5876.

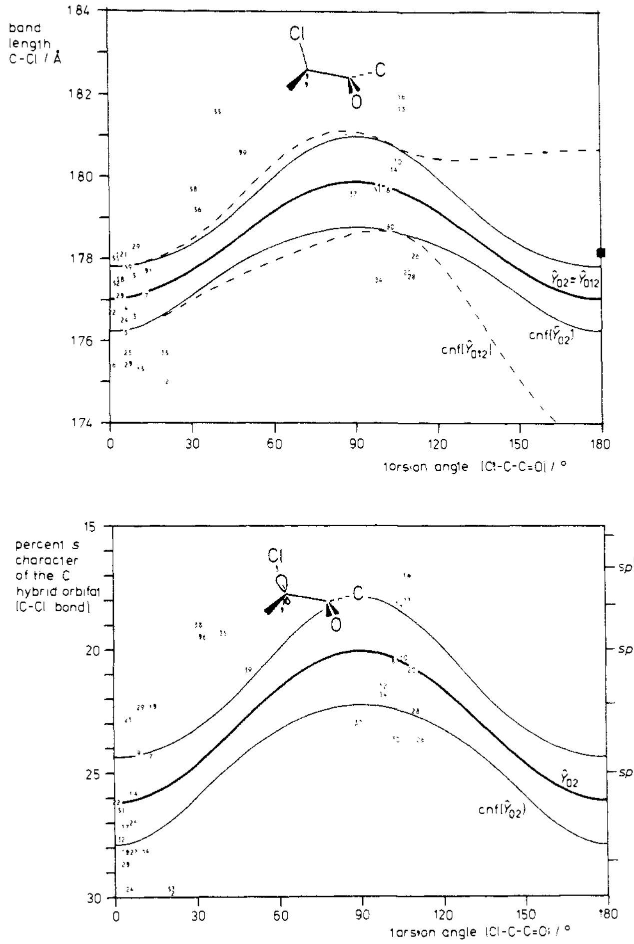

Figure 7. Bond lengths (upper diagram) and carbon hybrid orbital compositions[11] (lower diagram) of C—Cl bonds of α-mono- and α,α-dichlorinated ketones (X-ray data) plotted versus the absolute value of the torsion angle Cl—C—C═O/deg. The data are represented by their item numbers (see Table S7 of the supplementary material). Upper diagram: (■) chloroacetaldehyde;[47a] the cos ω term in $\hat{Y}_{012}$ is not significant.

teractions between the C—Cl and the C═O bond dipoles.[39-41] In preparative organic chemistry, several 2,2-dibromo-1,3-dicarbonyl compounds are used as mild brominating agents[42,43] (3″, R = Br). Beside these chemical facts, α-chloro ketones are interesting examples for hybrid orbital adjustments because the positions of the chlorine atoms can be well determined in X-ray structures without losing too much accuracy of the carbon and other lighter atom positions and because the C–Cl bond is very sensitive toward changes of carbon hybridization.[44,45]

The analysis of the X-ray structures of α-chlorinated ketones shows that the C—Cl bond lengths and the carbon hybridizations in C—Cl bonds exhibit a similar dependence[22] on the Cl—C—C═O torsion angle[46] as do the ketones (see Figure 7). To justify the adjustment of simple cos 2ω functions on the experimental data, the results of ab initio calculations on chloroacetaldehyde are shown in Figure 8 (the inclusion of other cos terms generates very large confidence intervals).

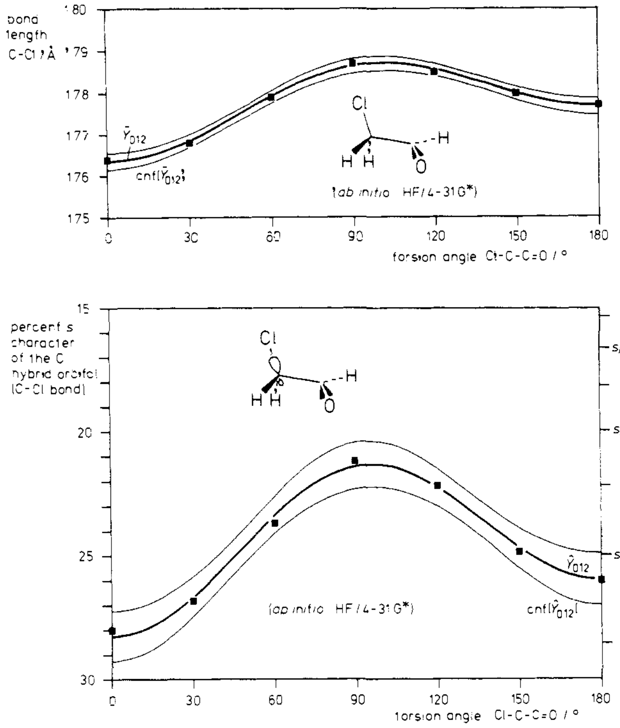

Figure 8. Carbon–chlorine bond lengths (upper diagram) and C hybrid orbital compositions[11b] of the C—Cl bond of chloroacetaldehyde as functions of the torsion angle Cl—C—C═O/deg. For numerical values, see Tables S8 and S9 of the supplementary material.

Table I. Potential Energy Barriers V_i (kcal/mol)[a]

molecule	V_1	V_2	V_3	ref
CH_3CH_2CHO	0.8	1.1	1.3	*b*
$ClCH_2CHO$	-2.4	1.7	1.3	this work
FCH_2CHO	-4.6	3.7	1.0	*c*

[a] See also: Reference 6. [b] Computed from the data in ref 21 and 48. [c] Computed from the data in ref 21.

In each case, the Cl—C—C═O torsion angle was constrained to a multiple of 30° and the geometry was optimized on the 4-31G* level. The results in Figure 8 show that the functions with two significant cos terms describe the system very well. Unfortunately, the experimental data in Figure 7 do not scatter on the whole ω range, and therefore, we are forced to use only functions with a twofold cos term[22] (this term is dominant in the functions in Figure 8; the onefold term in the function in the upper diagram of Figure 8 probably comes from a C–Cl bond shortening in the syn conformer, which reduces the molecular dipole moment). The only experimental information about a C—Cl bond in antiperiplanar arrangement to a C═O bond comes from the gas-phase structure of chloroacetaldehyde,[47a] C—Cl = 1.782(4) Å, and this

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(39) T.L. thanks Prof. Dr. Dieter Seebach for this hint.

(40) See for example: Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; Chapter 14.2.d, p 422.

(41) Because both α-mono- *and* α,α-dichlorinated ketones were included in our analysis, the possibility that we see only a chloro analogue anomeric effect at C_α can be excluded. For anomeric effects at fluorine-substituted atoms, see ref 29.

(42) Sekiya, M.; Ito, K.; Suzuki, K. *Tetrahedron* **1975**, *31*, 231. Bloch, R. *Synthesis* **1978**, *10*, 140. Grundke, G.; Keese, W.; Rimpler, M. *Chem. Ber.* **1985**, *118*, 4288.

(43) It is not clear whether the C–X bond of α-halocarbonyl compounds is finally cleaved heterolytically or homolytically (see discussions in ref 42). For photochemical reactions, see: Morrison, H. *Rev. Chem. Intermed.* **1987**, *8*, 125.

(44) Dobbs, K. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 4663.

(45) For the relationship between the C–Cl bond length and the C hybridization in the C–Cl bond, see the discussion in ref 11b.

(46) A similar analysis of the C–Cl bond lengths in α-chlorinated cyclohexanones has been performed: Bocelli, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1249. On the basis of the data available at that time, it was concluded that there is no significant difference between the $C–Cl_{eq}$ and $C–Cl_{ax}$ bond lengths. However, the data presented in Figure 7 are in agreement with those given in an earlier publication: Gaultier, J.; Hauw, C.; Lectard, A.; Metras, F.; Petrissans, J. *J. Mol. Struct.* **1973**, *18*, 403. With the classification axial ⇔ $90° \leq \omega \leq 115°$ and equatorial ⇔ $0° \leq \omega \leq 30°$ we obtain the average C–Cl bond lengths (with esd's) $\bar{l}_{ax} = 1.794 \pm 0.004$ Å and $\bar{l}_{eq} = 1.768 \pm 0.002$ Å. The 99% confidence interval of their difference is [0.013 Å, 0.040 Å] (Behrens–Fisher statistic: $n_1 = 13$, $n_2 = 22$, $\nu = 19.3 \Rightarrow t = 2.86$). For other spectroscopic differentiations between the conformers of α-halo ketones, see: Bonniol, A.; Galsomias, J.; Pétrissans, J. *C. R. Acad. Sci., Paris, Ser. C* **1979**, *288*, 407. Maury, C.; Bonniol, A.; Lere-Porte, J.-P.; Petrissans, J. *J. Mol. Struct.* **1987**, *159*, 217. Nogaj, B.; Schroeder, G. *Magn. Reson. Chem.* **1987**, *25*, 565.

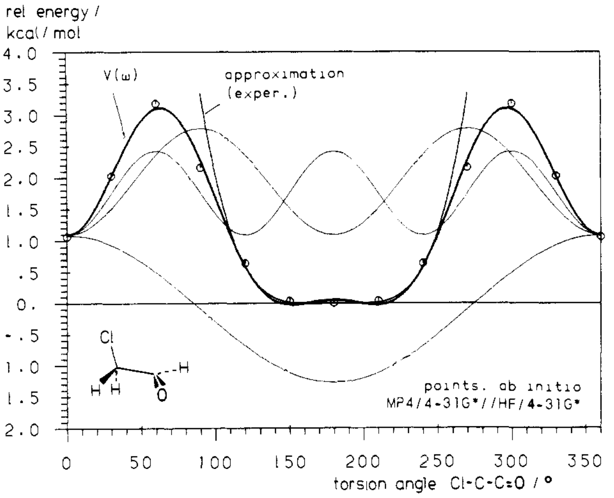

Figure 9. Relative energy of several conformations of chloroacetaldehyde (points). The adjusted function $V(\omega)$ (thick curve; the three cos components are vertically shifted and drawn as thin curves) agrees with the approximation for the potential energy function, which was experimentally determined for the anti conformer.[47] The double minimum about $\omega = 180°$ is confirmed by experiments, but exaggerated by $V(\omega)$.

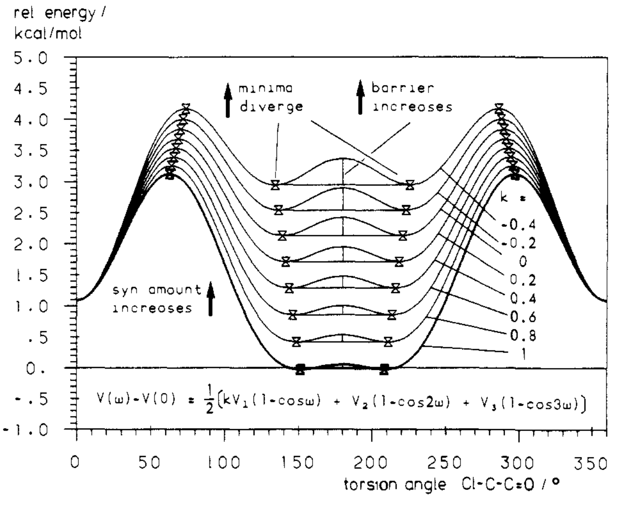

Figure 10. Qualitative illustration of a decrease of the influence of the dipolar term on the rotation barrier $V(\omega)$ of chloroacetaldehyde (decreasing parameter k). The thick curve ($k = 1$) represents the Fourier sum adjusted on the calculated energies of several conformations (see text and Figure 9). The local extrema with varying ω are designated. It is assumed that the V_2 and V_3 terms are not influenced by the solvent polarity.

value was included in the analysis of the bond lengths in Figure 7.

The calculated energies of the chloroacetaldehyde conformations are drawn as points in Figure 9. The least-squares adjustment of a truncated Fourier sum[36] $V(\omega)$ on the relative energies of several conformations yields V_i values that can be compared with those for propionaldehyde and fluoroacetaldehyde (see Table I). A comparison of the V_2 coefficients shows, as expected, that C–Cl hyperconjugation is energetically less favorable than C–C and more favorable than C–F hyperconjugation, and they all are less favorable than C–H hyperconjugation (each single V_2 value of a XCH_2COR molecule describes approximately the difference between the C–X and C–H hyperconjugative resonance energies).

Figure 10 explains qualitatively the different conformational behavior of chloroacetaldehyde in the gas phase[47] (anti conformer most stable) and in condensed phases[49] (syn and gauche conformers present; the syn conformer predominates in solvents of high dielectric constant). The ab initio potential energy curve (thick curve; $k = 1$) describes the gas-phase situation; in order to simulate a polar environment in the condensed phases, we have reduced the V_1 part in the Fourier series step by step, because the dipolar part of V_1 becomes less important in polar solvents.[40] It is conceivable that V_1 even becomes positive (negative k), as in propanal where the steric part dominates the V_1 term. As experimentally observed on going to more polar solvents, the amount of the syn conformer in the equilibrium increases and becomes preponderant. Simultaneously, the torsion angle difference for the two gauchelike conformers becomes bigger and the energy barrier between them grows (a threefold rotation barrier is observed in solutions[49]).

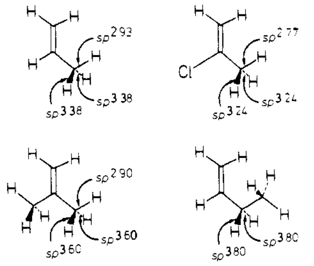

Figure 11. Carbon hybridizations[11b] in the allylic C–H bonds of the experimentally determined structures of propene,[55] 2-chloropropene,[56] isobutene,[57] and 1-butene.[58]

It seems reasonable to conclude that the C–Cl hyperconjugation in α-chlorocarbonyl compounds is a destabilizing resonance effect, but, depending on the polarity of the environment and the steric effects within the molecule (V_1 term), conformations with a Cl—C—C=O torsion angle between 90 and 120° are sometimes enforced, because in spite of the destabilizing hyperconjugation an overall stabilization results.

α-Nitro Ketones. Hartshorn and co-workers[50] have performed X-ray structure analyses of many nitration products of phenols. Those molecules that contain the fragment of an α-persubstituted ketone were included in the analysis of the bond lengths and hybridizations. The C—N bond lengths[51] exhibit a scattering similar to the C—Cl bond lengths in the α-chlorinated ketones, but do not vary with the torsion angle N—C—C=O. On the other hand, the C hybridization in the C—N bond depends doubtless on the N—C—C=O torsion angle in the expected way. There is no obvious explanation for this contradiction between the behavior of the bond lengths and the hybridizations, but it should be noted here that the situation is more complicated due to the ability of nitrogen to form C–N double bonds and the fact that the nitro group contains a π system itself, which can be regarded as a heterocarbonyl system (see Figures S4 and S5 of the supplementary material). The C_α–C_β bonds of the nitro ketones behave similarly as in the ketone case: only the C_α hybridizations have a significant cos 2ω component.

Allyl and Benzyl Chlorides. The first evidence for carbon–chlorine hyperconjugation came from studies of the polarizability of benzo trichloride[52] and the analysis of photoelectron spectra of allyl and benzyl halides.[53] We have analyzed the X-ray structures of several allyl and benzyl chlorides, but unfortunately, only few structures of sufficient precision are available to date. Both the C–Cl bond lengths and the C hybridizations show a considerable scattering. It is possible to adjust a simple cos

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(47) (a) Dyngeseth, S.; Schei, H.; Hagen, K. *J. Mol. Struct.* **1983**, *102*, 45. (b) Ford, R. G. *J. Chem. Phys.* **1976**, *65*, 354.

(48) van Nuffel, P.; van den Enden, L.; van Alsenoy, C.; Geise, H. J. *J. Mol. Struct.* **1984**, *116*, 99.

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(50) Hartshorn, M. P.; Robinson, W. T.; Vaughan, J.; White, J. M. *Aust. J. Chem.* **1985**, *38*, 575, and references cited therein.

(51) The C–N bond lengths lie in the same range as in other tertiary nitro compounds; see, for example: Kai, Y.; Knochel, P.; Kwiatkowski, S.; Dunitz, J. D.; Oth, J. F. M.; Seebach, D.; Kalinowski, H.-O. *Helv. Chim. Acta* **1982**, *65*, 137.

(52) Aroney, M. J.; Calderbank, K. E.; Le Fèvre, J. W.; Pierens, R. K. *J. Chem. Soc. B* **1970**, 1120.

(53) Schmidt, H.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 307. Schmidt, H.; Schweig, A. *Tetrahedron Lett.* **1973**, 981.

function on the bond lengths as a function of the torsion angle, which exhibits the behavior expected for a hyperconjugative interaction of the C–Cl bond with the π system, whereas the adjustment of a corresponding function on the hybridizations shows no significant dependence on the torsion angle. Probably the steric interactions falsify the hybridizations (see Figure S6 of the supplementary material).

Molecules with Allylic C–H Bonds. In order to minimize the influence of steric interactions, we have analyzed the data of several small molecules whose structures were determined with high precision by electron-diffraction or microwave spectroscopy. Only those molecules were considered for which the geometry of the allylic methyl or methylene group was determined with as few constraints as possible[54] (i.e., only a local mirror plane was assumed). In all cases, one obtains C hybridizations for the allylic C–H bonds that fit into the model of hyperconjugative interaction with the π system: the p character of the in-plane C–H bonds is smaller than that of the out-of-plane C–H bonds (see Figure 11). In the allylic methyl groups the larger C–H bond lengths[59] correlate with the higher p character of the C hybrid orbitals in the C–H bonds. This observation is in agreement with the results from IR spectroscopy, which prove that methyl groups adjacent to a trigonal carbon atom have one stronger (in-plane) and two weaker (out-of-plane) C–H bonds.[60]

Ab Initio Calculations

Complete geometry optimizations have been carried out with the 4-31G* basis set[61] for 2-chloroacetaldehyde and with the 3-21G* basis set[62] for isopropylamine. The 4-31G* set for the Cl atom was formed by combining the same polarization function (*d*) of Cl used for the 6-31G* representation with the corresponding 4-31G set. Similarly, the 3-21G* set for the first-row elements was formed by combining the 3-21G set with the *d* polarization function out of the corresponding 6-31G* set. In order to obtain quantitatively more reliable energy differences for the internal rotations for both molecules, the Møller–Plesset perturbation theory up to fourth order (MP4) was used in conjunction with the 6-31G* basis set.[61] The geometry optimizations were performed with the MONSTERGAUSS program system,[63] and the MP4 calculations were carried out with the GAUSSIAN 82 suite of programs.[64]

Conclusions

The calculation of the hybrid orbital compositions of tetrahedral carbon atoms adjacent to trigonal atoms from the experimentally (or computationally) determined geometry of an unstrained molecule by least-squares adjustment yields a new confirmation for the dependence of bond properties on torsion angles. The results can be interpreted in terms of hyperconjugative interactions between the tetrahedral and the trigonal atoms.

Acknowledgment. We thank Prof. Dr. Dieter Seebach for generous financial support, Prof. Dr. Alfred Bauder for interesting and helpful discussions, and Dr. Stefan Müller for CAS ONLINE literature searches.

Registry No. $(CH_3)_2CHNH_2$, 75-31-0; $ClCH_2CHO$, 107-20-0.

Supplementary Material Available: Tables of geometric parameters and computed hybrid orbital compositions depicted in Figures 2–4 and 7 (with references to the original publications) and of the results of the ab initio calculations and seven figures (27 pages). Ordering information is given on any current masthead page.

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[54] Many structures of small molecules with methyl groups at trigonal carbon atoms, listed in *Landolt-Börnstein*, New Series, Group II; Springer-Verlag: Berlin, 1976; Vol. 7, p 108, were refined with more constraints (local C_{3v} symmetry; equal H–C–H angles). In these cases only uninterpretable results, which stand in contradiction to those from the less constrained structures, were obtained.

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[64] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, G.; Pople, J. A. *GAUSSIAN 82 Program System*; Carnegie-Mellon University: Pittsburgh, PA, 1983.