methyl derivative of the latter group of complexes.[46] Furthermore, Costa and coworkers[47] have demonstrated independence of rate with respect to incoming ligand concentration for anation reactions of alkylaquo-1,3-bis(biacetylmonooximimino)propanatocobalt monocation (a complex quite similar to the alkylcobaloximes) in a solvent of 1% water in acetone which has been interpreted in terms of a limiting SN1 mechanism. Finally, the extensive work of Hill and coworkers has provided evidence for the existence of pentacoordinate species among the alkylcobinamides and alkylcobalamins from the temperature dependence of uv, visible, and pmr spectra,[48] and from correlation of similar studies plus CD spectra with data on the thermodynamics of ligand substitution of numerous cobalt–corrin complexes.[49,50]

It may well be impossible to demonstrate the kinetic criterion for the SN1 mechanism since the rate for the dissociation of water from $Me(D_2H_2)HOH$ (k_1, eq 15) may be extremely fast, causing the rates of ligation to become experimentally inaccessible before saturation can be achieved. Furthermore, the clear possibility exists that at room temperature the cobalt complex may exist predominately as the pentacoordinate $Me(D_2H_2)$ species, in which case the reaction with thiols may be better described as ligand addition rather than substitution (eq 16a and 16b). In support of this possibility, Hill and coworkers[48] estimated that methylcobinamide exists 90% as the pentacoordinate species in water at 20°.

If either the SN1 mechanism of ligation (eq 15, 16a, and 16b) or the bimolecular mechanism of ligand addition to $Me(D_2H_2)$ (eq 16a and 16b) is indeed applicable, then the greater reactivity of neutral thiol over thiolate anion in this system may be attributed to the importance of π bonding in the transition states for reactions 16a and 16b. The neutral ligands, RSH and $RSCH_3$, would be expected to act as better π acceptors than thiolate anion,[51] and although the stabilities of the complexes formed from the former compounds are far lower, the rate constants for ligand substitution are greater. A significant contribution of π bonding to the transition states for these reactions would also provide an explanation for the almost total lack of dependence of substitution rate on thiolate anion basicity, since an increase in basicity would be expected to make a thiolate anion a better σ donor, but, compensatingly, a poorer π acceptor. A similar involvement of π bonding in the ground state for the thiolate anion complexes might also explain the observed increase in the equilibrium constants for ligation by thiolate anions compared to substituted pyridines, as well as the decrease in sensitivity of the equilibrium constants to ligand basicity for the thiolate anions ($\beta = 0.18 \pm 0.01$) as opposed to substituted pyridines ($\beta = 0.29 \pm 0.02$) (Figure 7).

Further work is in progress in an attempt to substantiate the proposed SN1 mechanism for ligation reactions of $Me(D_2H_2)HOH$ and to assess the relative importance of π bonding in trans-liganded complexes containing alkylcobalt bonds.

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Effect of Steric Hindrance on the Structure of Transition States[1,2]

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Abstract: From chlorine isotope effects in the Menshutkin reactions of triethylamine ($k^{35}/k^{37} = 1.00640 \pm 0.00009$) and quinuclidine ($1.00709 \pm 0.00011$) with methyl chloride in 1,2-dimethoxyethane solution at 25°, steric strain evidently *decreases* during passage through the transition states for these reactions, thereby causing the former reaction to have the earlier (more reactant-like) transition state. This is attributed to relatively rapid motion of the hydrogens on the flattening methyl at the transition state. Analogies to oxonium, carbonium, and enolate salt formation are noted.

No definitive information has been published concerning the effect of purely *steric* structural changes of reactants on the structure of transition states, although several rules for predicting the effect of predominantly *electronic* changes on transition-state geometry have been proposed and experimentally tested.[4–10]

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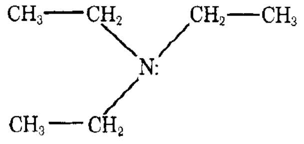
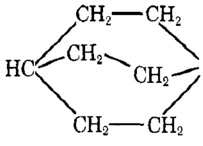
The purpose of the present study was to determine experimentally the effect of changes in steric hindrance on the structure of transition states in typical polar reactions in which all factors except steric hindrance (*e.g.*, basicity of nucleophile, acidity of electrophile, temperature, and solvent) are constant, with the hope of rationalizing the results and using them to predict sterically induced transition-state differences in other systems, including ones where steric and electronic differences coexist.

The Menshutkin reaction[11–13] of tertiary amines with methyl halides to give quaternary ammonium salts was chosen as a model reaction because it has already been studied extensively in other respects, is a typical simple bimolecular polar reaction, is cleanly second order, and is suitably sensitive to the size and disposition of the alkyl groups attached to nitrogen, being less than 0.4% as fast with triethylamine (**1**) as with quinuclidine (**2**) under typical conditions.[14] This lower rate with **1** than with **2** must be attributed almost entirely to steric hindrance because the measured basicities (pK_a of conjugate acid in H_2O at 25°) of **1** (10.75,[15] 10.67[16]) and **2** (10.95)[17] are practically identical, probably the same within experimental error. From molecular models, it is apparent that **1** in solution must prefer a conformation in which the methyl moiety of one ethyl group extends forward while the other two ethyl groups occupy a rear position, giving it a steric bulk similar to that of 2-methylpyridine. On the other hand, **2** has a very exposed nitrogen and is an excellent nucleophile, and its complexes are very stable.[12]



1



2

The problem, then, is to decide which of **1** and **2** has the later (more product-like, stronger N–CH_3 bond) transition state. Prior predictions generally favored **1**, on the basis that the products are more strained than the reactants; hence strain might be expected to increase along the reaction coordinate. Since the transition state is defined as the structure of highest energy along the easiest path from reactants to products, greater strain in the transition state with **1** should therefore lead to a more product-like transition state for **1** than for **2**. In other words, since the product with **1** is harder to form, it needs a relatively stronger N–C bond before completion of N–C bonding is assured.

To determine the answer *experimentally*, we resorted to an indirect method, comparison of the chlorine isotope effect of **1** *vs.* **2** to compare the relative extents of weakening of the C–Cl bond of methyl chloride (loss of zero-point vibrational energy due to lowered force constants) at the two transition states. Decreased bond orders and increased bond lengths are associated with lower force constants.[18] The assumptions are made (1) that the CH_3 group has minimal ability to stabilize positive or negative charge (therefore increased N–C bond strength should be accompanied by complementary weakening of the C–Cl bond to preserve a nearly constant sum of bond orders around the methyl carbon) and (2) that this should be reflected in a larger measured k^{35}/k^{37} chlorine isotope effect. The natural abundances of ^{35}Cl and ^{37}Cl are sufficient for isotope effect measurements, and substituent effects on chlorine isotope effects have been reported previously for other reactions.[19]

To avoid possible complications due to strong solvation of the chloride or desolvation of the amine, we studied these reactions in a solvent that interacts extremely weakly with anions and amines, 1,2-dimethoxyethane, hereafter called DME.[20]

Results and Discussion

Table I records rate constants for these reactions. To be consistent, each deviation (± value) reported in this paper is a $\sigma_{\bar{x}}$, *i.e.*, a standard deviation of the mean ($\bar{x}$ value) to which it is appended.[21] Compound **1** reacts only 0.37% as fast as **2** with methyl chloride in DME at 25°. The changes in heat and entropy of activation from 10.00 ± 0.34 kcal mol^{-1} and −38.5 ± 1.1 gibbs for **2** to 11.87 ± 0.13 kcal mol^{-1} and −43.4 ±

Table I. First-Order Rate Constants for Reaction of 0.2 *M* Tertiary Amines with 2.0 *M* CH_3Cl in DME

Amine	Run no.	Temp, °C	10^6k_1, sec^{-1}	Mean 10^6k_1, sec^{-1}
1	81	25	7.99	
	82	25	8.21	8.11 ± 0.06
	83	25	8.14	
	90[a]	25	7.3[a]	
	87	0	1.16	1.19 ± 0.03
	92	0	1.22	
2	84	25	2360	
	85	25	2000	2170 ± 110
	86	25	2160	
	88	0	432	425 ± 7
	89	0	417	

[a] Run with added glass wool; standard deviation of k_1 calculated for each point in run 90 is ±0.2.

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Table II. Chlorine Isotope Effects for Reaction of Tertiary Amines with 2.0 M CH_3Cl in DME at 25°

Amine	Run no.	Reaction,[a] %	Measurement[b] no.	k^{35}/k^{37}	Av k^{35}/k^{37}
1	40	10.8	1	1.00649	1.00643
			2	1.00637	
	41	10.5	1	1.00622	1.00612
			2	1.00601	
	42	10.4	1	1.00667	1.00646
			2	1.00625	
	52	4.15	1	1.00636	1.00632
			2	1.00605	
			3	1.00655	
	53	4.40	1	1.00688	1.00668
			2	1.00679	
			3	1.00652	
			4	1.00654	
2	43	10.3	1	1.00710	1.00696
			2	1.00683	
	44	10.1	1	1.00677	1.00674
			2	1.00671	
	45	10.2	1	1.00733	1.00714
			2	1.00696	
	54	4.60	1	1.00726	1.00738
			2	1.00743	
			3	1.00745	
	55	4.81	1	1.00697	1.00723
			2	1.00748	
			3	1.00724	

[a] Per cent of CH_3Cl reacted, calculated from the amount of amine added to the reaction mixture. [b] Independent mass spectral analyses on reactant and product CH_3Cl samples.

0.4 gibbs for **1** contribute about equally to the reduction in rate, presumably because extra work must usually be done to rotate back at least one methyl end of an ethyl group in **1**, whereas the alkyl chains are permanently locked in a noninterfering conformation in **2**.

Table II records chlorine isotope effects k^{35}/k^{37} for these reactions at 25°. The mean of the average values is 1.00640 ± 0.00009 for **1** *vs.* 1.00709 ± 0.00011 for **2**. Comparison with an observed isotope effect for halide exchange under the same conditions (1.00862 ± 0.00010),[3,22] which should have an approximately symmetrical transition state with a half-broken C–Cl bond, or with the calculated maximum isotope effect of 1.017[23] for complete breaking in a solvent providing negligible solvation for chloride ion, indicates that both Menshutkin transition states are closer to reactants than products in structure; *i.e.*, they have "early" transition states. This conclusion agrees with that deduced from small values of the difference between solvent effects on free energies of reactants and free energies of activation,[24] although it is opposite to earlier views that Menshutkin transition states are product-like.[25]

The more remarkable result is the fact that the isotope effect is smaller for **1** than for **2**, with greater than 99% statistical probability, indicating that **1** has the earlier, rather than the later, transition state, of the two amines. This seems to necessitate the following interpretation.

At and near the transition state, crowding is being relieved and steric strain is decreasing during translation along the reaction coordinate in the direction of products. This steric factor due mostly to interactions between nonbonded hydrogens (on amine and methyl) is only one of many contributions determining the energy at any point along the reaction coordinate. However, if it adds relatively more energy to earlier (more reactant-like) points, such increased crowding causes the transition state to come earlier, because the transition state is defined to be at the point of maximum energy, not at a minimum.

This deduction that steric strain *decreases* during passage through the transition state at first sight appears to be in conflict with the fact that steric strain is higher in the product than in the reactant. However, it is evidently higher still at the transition state, in which case the crux of the problem is whether the transition state comes on the ascending or descending side of the curve for strain energy *vs.* reaction coordinate. These results imply that it is on the descending side.[26]

In this Walden inversion, the incipient bonding of nitrogen to carbon initiates lengthening of the carbon–chlorine bond and consequent flattening of the methyl. The flattening and subsequent inversion are certainly due more to approach of the nitrogen electron pair and separation of chloride ion than to any steric crowding between nonbonding hydrogens. Nevertheless, let us consider the small perturbation due to steric hindrance. Very early in the process, steric crowding must increase as the N–C distance shortens without much angular change for the methyl hydrogens. However, we interpret the above results to mean that, at the transition state, the methyl hydrogens are at last moving forward faster than nitrogen is approaching the methyl carbon, thereby widening the gap between the methyl hydrogens and the nearest hydrogens of the tertiary amine that are responsible for the greater crowding at an earlier stage. This must be true even though the geometry of CH_3 is probably still short of coplanarity as judged by the small chlorine isotope effects for both.

Extension of these conclusions to reactions of hindered hydroxylic nucleophiles with primary or secondary halides or sulfonate esters is probably valid because such alcoholyses and solvolyses are mechanistically similar to the Menshutkin reaction.

Furthermore, it is likely that many rate-determining ionization reactions yielding carbonium ions or enolate ions involve a similar lessening of crowding between nonbonded hydrogens. Thus the transition state for ionization of a tertiary alkyl chloride with bulky crowded groups to a carbonium chloride resembles the Menshutkin reaction in respect to relief of strain during passage through the transition state, which should also be reached just short of coplanarity (although in respect to magnitude of charge development, solvent

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[22] Mean of 1.00872, 1.00841, and 1.00872 for three runs with 0.2 M NaI and 2.0 M CH_3Cl, each to 8.59% conversion of CH_3Cl to NaCl in DME at 25°.

[23] Two-atom model at 298°K, CH_3 treated as a point mass of 15 atomic mass units, 3.4 mdyn/Å force constant for C–Cl bond, bending neglected.

[24] M. H. Abraham, *Chem. Commun.*, 1307 (1969); 293 (1970); also variations of free energy of activation with solvent[11] are less than half as large as for solvolyses of *tert*-butyl chloride.

[25] Reference 4, p 417.

[26] Strictly speaking, the experiments require only that the strain energy of the **1**–CH_3Cl system be decreasing relative to that of the **2**–CH_3Cl system at their transition states; a decrease for the former and increase for the latter would also fit, but seems unlikely with such a small structural change.

effects, and electronic substituent effects it is much more extreme). Similar relief of strain during flattening around carbon may occur in many base-induced enolizations. A common feature in all of these reactions may be a relatively large rate of displacement of atoms or groups attached to the flattening carbon at the transition state.

Note that these are *not* the predictions that one would make by considering simply the enthalpy or free energy of reaction of the rate-determining step. For example, the ionization of a tertiary alkyl chloride to a carbonium chloride is endothermic and endergonic, quite the reverse of the Menshutkin reaction, yet we are making the *same* prediction for the two types. The similarity is in the transition states, not in the first products. Our viewpoint contrasts with usual thermic postulates, which often give wrong predictions for the effect of central carbon substitution.

Note also that the principle of microscopic reversibility requires that, if steric strain decreases during passage through the transition state in the directions described, it must increase for the reverse reactions of these quaternary ammonium, oxonium, carbonium, or enolate ions, or closely analogous reactions.

Experimental Section[2,3]

Preparation of Starting Materials. Sources and preparation of triethylamine (**1**), CH_3Cl, and the solvent 1,2-dimethoxyethane (DME) have already been described.[2,3] Inorganic chemicals were reagent grade.

Quinuclidine (**2**) was prepared by dissolving its hydrochloride (Aldrich) in a minimum of water and neutralizing with 50% NaOH solution. This mixture was extracted several times with reagent ether. The ether extracts were combined and carefully evaporated to a thick solution on a Büchi rotary evaporator. The extreme volatility of **2** makes this step hazardous. The solution was introduced in aliquots sufficient to cover the bottom of a large sublimator. The last traces of solvent were carefully removed under house vacuum (180 Torr) in the sublimator. The **2** was then sublimed at 25° using Dry Ice–ethanol to cool the trap, mp 158.1–158.8° (sealed tube, corrected) [lit.[27] mp 158°].

Isotope Effects. The chlorine isotope effects for reactions of **1** and **2** with CH_3Cl are given in Table II. The procedure for their measurement has been described[3] and the observed ratios are recorded elsewhere.[2,3] Temperature control was to ± 0.05° in an ice-packed dewar at 0.00°, in a large water bath at 25.00°, or in an oil bath at 50.00°.

The isotope effects and their associated errors for **1** and **2** were submitted to the *t* test for significance. The probability is greater than 0.99 that **2** has the larger k^{35}/k^{37}.

Systematic Errors. Additional experiments were run to decrease the likelihood that the difference in isotope effects between **1** and **2** is due to an experimental artifact. The sealed tubes containing the reaction mixture were warmed from −80 to 25° to start the reaction. Since **2** reacts so rapidly, a significant fraction of this reaction might have occurred at lower temperatures. The isotope effect for a given reaction is expected to increase with decreasing temperature.[28] This situation could contribute to the higher isotope effect observed for **2**. Isotope effects for **2** at 0 and 50° do indeed display a temperature dependence in the direction predicted by theory and required to explain the results (Table III). Therefore two isotope effect runs for **2** were carried out by a modified procedure that allowed the reagents to be mixed and to react at 25° (59 and 60, Table III). The isotope effects for these runs are within experimental error of those carried out by the usual procedure (Table I). Thus a temperature effect is not responsible for the observed difference in isotope effects for **1** and **2**.

For these runs (59 and 60) it was desired to mix the reactants (and run the reactions) at 25° instead of warming the tubes from Dry Ice–ethanol temperature. The procedure and apparatus were modified as follows. The reaction tubes had a large-bore stopcock in place of the constriction. Only a small stem was retained on the open side of the stopcock. This stem was fitted with a no-air stopper. CH_3Cl and DME were introduced as before. The stopcock was opened to admit syringe needles. The tube and its contents were warmed to 25°. A measured volume of stock solution of **2** in DME was then quickly added by syringe. The stopcock was closed quickly and the tube shaken vigorously. Other aspects of the procedure were the same as described previously.[3]

Table III. Effect of Temperature on Chlorine Isotope Effect for Reaction of 0.1 *M* **2** with 2.0 *M* CH_3Cl in DME

Run no.	Temp, °C	Measurement no.	k^{35}/k^{37}	Mean
57	0	1	1.00771	
		2	1.00773	1.00771
		3	1.00770	
59	25	1	1.00687	1.00698
		2	1.00709	
60	25	1	1.00706	1.00700
		2	1.00693	
50	50	1	1.00652	
		2	1.00672	1.00665
		3	1.00672	

The difference in isotope effects between **1** and **2** cannot be attributed to a difference in basicity (an "electrical" factor). Values of pK_a, given above, are probably within experimental error of one another. If the small measured difference is real and the conjugate acid of **2** has a higher pK_a (more basic), the effect would be a smaller chlorine isotope effect for **2** (in the wrong direction).

Slow mixing in the case of the reactive **2** can also be excluded as the source of the difference. The speed of this reaction is not so rapid that the reagents could not be thoroughly mixed in a time very short compared to the half-life of the reaction (about 5 min). If mixing were slow, the effect would be to lower the isotope effect for **2** (in the wrong direction).

Kinetics. Since some cases of autocatalysis[29] and possible surface catalysis[30] are known for the Menshutkin reaction, kinetic studies were made that confirmed their absence in the present work.

The results of kinetic measurements for reactions **1** and **2** with CH_3Cl are given in Table I. The first-order rate constants did not vary as far as the reactions were followed (80–90% completion). This constancy shows that there is no autocatalysis. That there was no surface catalysis by glass was demonstrated by addition of glass wool to the ampoules in one run (90) for **1**. The slightly slower rate constant for this run is probably due to some loss of CH_3Cl.

The original kinetic data for 11 kinetic runs are recorded elsewhere,[2] with chronological run number, time, and titer in milliliters of 0.453 *M* $AgNO_3$ for each point, and time and temperature for the measured infinity point of each run. Details of the procedure are the same as those for the isotope effect runs. A number of 2-ml ampoules (Kimble Neutraglas) were capped with 8-mm no-air stoppers and flushed with dry N_2. CH_3Cl (0.2 ml, 0.198 g, 4 mmol) was condensed into the ampoule, the amount being measured by comparison to another ampoule containing 0.2 ml of a liquid. Then 1.8 ml of a 2.22 *M* stock solution of amine (**1** or **2**) was added by syringe to the cooled ampoule. The ampoule was sealed with a flame and stored in a Dry Ice–ethanol slurry until all ampoules for a run had been prepared. At zero time the ampoules were simultaneously warmed to the reaction temperature and placed in the appropriate bath. At intervals the ampoules were removed from the bath and cracked open and the contents suction filtered on a small Büchner funnel. The vial and the filtered residue were rinsed into a 50-ml flask with 15 ml of water. To this flask were added a small amount of $CaCO_3$, 0.1 g of dextrin (Eastman pure), and two drops

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of dichlorofluorescein indicator (0.1% in 70% aqueous ethanol). The resulting mixture was titrated to a pink end point with 0.0453 *M* $AgNO_3$ solution.[31] For early points with small titer, 5 ml of 0.01678 *M* NaCl (dried at 120° for 12 hr) solution was added by pipet to make the end point easier to see. The titer for this NaCl (1.85 ml) was subtracted from the observed titer to obtain the titer due to product. Infinity points were taken after at least 10 half-lives either at reaction temperature or at some higher temperature. The rate constant for a run is the average of first-order rate constants calculated for each point.

In one run (90) 0.05 g of Pyrex No. 7220 glass wool (Corning No. 3950) was forced into each ampoule after the CH_3Cl had been introduced. Although care was taken not to contact the liquid CH_3Cl, some loss no doubt occurred, since removal of the stopper for several minutes was necessary. For sampling, the ampoule was cracked open and the glass wool removed by a forceps and placed on the filter. The remaining contents of the ampoule was filtered and then the glass wool was tamped. In other respects this run was carried out just as the others.

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Conformational Dependence of Homoallylic H–H Coupling Constants

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Abstract: A theoretical study of the conformational dependence of long-range H–H coupling over four single bonds and one double bond (homoallylic coupling) is presented in terms of the semiempirical valence-bond (VB) theory as well as self-consistent perturbation theory in the INDO (intermediate neglect of differential overlap) approximation of the self-consistent-field molecular orbital (SCF–MO) formalism. Either of these theoretical formulations provides an adequate description of the conformational dependence of homoallylic H–H coupling in molecules of rigid geometry and can be used in the solution of stereochemical problems. However, the INDO–MO method, which includes all of the valence electrons, correctly predicts that the homoallylic coupling constants in *trans*-2-butene should be larger than in *cis*-2-butene. The VB method, which only included the π-electron mechanism, gives identical coupling constants for these two molecules. The advantage of the INDO–MO method arises because the inclusion of all valence electrons gives rise to additional mechanisms. For example, a comparison of the VB and MO results indicates that the major factor responsible for the differences between cisoid and transoid homoallylic coupling constants is a *direct mechanism of negative sign*, which arises for *cis*-2-butenes because of the proximity of the bonds containing the coupled nuclei. A discussion is also given of the effects of substituents on the magnitude of the homoallylic coupling constants.

Nuclear spin–spin coupling constants over four single bonds and one double bond are said to be of the homoallylic[2] type between protons H_A and H_B in the system $H_A—C_1—C_2=C_3—C_4—H_B$ with carbon atoms C_1 and C_4 having tetrahedral hybridization. Although this type of coupling has been observed extensively,[3–6] theoretical studies[7–10] have dealt with this type of coupling as only one aspect of the general long-range coupling constant phenomenon in which the dominant mechanisms are σ–π configuration interaction (exchange in valence-bond terminology) and delocalization in the π-electron system. For a C–H bond β to the double bond the interaction has a $\sin^2 \phi$ dependence on the dihedral angle, ϕ. Since there are two such interactions in the homoallylic fragment, this type of coupling constant should have a $\sin^2 \phi \sin^2 \phi'$ dependence on the dihedral angles ϕ and ϕ'. Both of these angles are measured in the same sense relative to the plane formed by the four carbon atoms of the 2-butene fragment. This situation is depicted in Figure 1. An angular dependence of this type is entirely consistent with the gross features of homoallylic H–H coupling[3–6] but it does not account, for example, for the well-documented difference between the homoallylic coupling constants in *cis*- and *trans*-2-butenes.[11,12] These differences have been attributed to contributions from a σ-electron mechanism, which will be larger for the all trans arrangement of the bonds linking the coupled nuclei.[13,14]

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(11) The terms cisoid and transoid will be used in this study to distinguish between the cases in which the coupling is associated with molecules in which the C_1 and C_4 carbon atoms are on the same or opposite sides of the double bond, respectively. These terms are used consistently to avoid confusion with cis and trans coupling constants in cyclic systems. For notational convenience, cisoid and transoid coupling constants will be differentiated in the left superscript, *i.e.*, ${}^{5c}J_{HH'}$ and ${}^{5t}J_{HH'}$.

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