conformations. However, open-chain binaphthyls can exist for a given absolute configuration in cisoid and transoid conformations of opposite helicity. Our results demonstrate that the sign of β_M is determined by the dihedral angle between the two aromatic parts. Therefore it is possible to determine the conformation of biaryls from the sign of their twisting power: cisoid conformations giving right-handed cholesterics and transoid conformations left-handed cholesterics for the *S* absolute configuration.

Experimental Section

Pitch values were measured at room temperature by means of the "droplet method"[19] using a Leitz Ortholux microscope and/or with the "lens" version of the Grandjean–Cano method[20] using a Zeiss Standard 16 microscope.

Helical handedness was determined from the sign of the rotatory power[21] and from the sense of the spiral-like disclination observed under circular boundary conditions.[22]

The linear dichroism and average absorption spectra were recorded by a modulated technique with a JASCO J-500A spectropolarimeter equipped with LD attachment. The liquid crystalline matrix was obtained by using a bicyclohexyl nematic, transparent to the UV radiation (ZLI 1167 from Merck) and a surface coupling agent in order to get linearly anisotropic samples (the experimental details are discussed in ref 23).

The CD spectra were recorded at room temperature with a JASCO J-500A spectropolarimeter equipped with a DP-500 data processor. Absorption spectra were recorded with a JASCO UVIDEC-510 spectrophotometer and/or a Varian DMS 90 spectrophotometer.

Compounds **4**[16a] and **8**[24] were kindly supplied by Professor S. F. Mason. Compound **1** was a commercial product. Compounds **7**, **9**, and **10** were kindly supplied by Dr. J. P. Mazaleyrat.[25] Molecules **3**, **5**, and **6** were kindly supplied by Dr. M. Hibert and **2** by Dr. Welwart.

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We are grateful to Professor S. F. Mason for derivatives **4** and **8**, Dr. J. P. Mazaleyrat for compounds **7**, **9**, and **10**, Dr. M. Hibert for compounds **3**, **5**, and **6**, and Dr. Welwart for molecule **2**.

Registry No. **1**, 18531-99-2; **2**, 76373-23-4; **3**, 51751-91-8; **4**, 18531-95-8; **5**, 75640-87-8; **6**, 99747-67-8; **7**, 99764-91-7; **8**, 32587-64-7; **9**, 37803-02-4; **10**, 98834-91-4; K15, 40817-08-1; E7, 63748-28-7.

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Transannular Interactions in Difunctional Medium Rings. 1. n/π Interactions in Cyclic Amino Ketones and Aminoalkenes Studied by Photoelectron Spectroscopy

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The He I photoelectron spectra of the cyclic and bicyclic amino ketones **1–4** and aminoalkenes **5–8** have been recorded and interpreted with respect to transannular interactions of the functional groups. The interactions have been determined by comparing the spectra of **1–8** with those of the monofunctional compounds **9–20**. For **1–4** the n_O ionization can be considered as an indicator of transannular interaction. For **5–8** the amount of interaction is measured by the shifts of the n_N and the π_{CC} orbitals. The results indicate considerable n/π interactions in the eight-membered rings of **2** and **6**. Of the compounds with a ten-membered ring, there is only interaction in amino ketone **3**, while it is virtually absent in aminoalkene **7**. Conformations are proposed to account for these findings.

Transannular interactions[1-3] are of prominent importance for the structure and the reacivity of medium-sized cyclic compounds. The existence of certain conformations, in which opposite sides of the ring come into close proximity to each other, is a unique feature of medium-ring structure.[1] Transannular reactions are frequently observed for ionic, free radical, and carbenoid attack on unsaturated medium rings, and also transannular cycloaddition is observed in appropriate systems.[2] The chemistry of compounds with two functional groups may be dominated by transannular interactions between the functionalities.[2] Due to the restricted flexibility of a cyclic molecule, the relative positions of the interacting groups can be estimated to a higher degree than in analogous acyclic molecules or in systems composed of monofunctional molecules. As has been expressed by the structure-correlation method of Dunitz and Bürgi,[4] intramolecular interactions can serve as models for intermolecular interactions.

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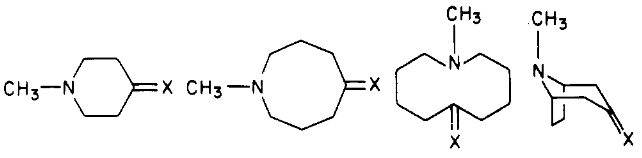
Table I. Vertical Ionization Potentials (IP_v, eV) of Amino Ketones 1–4, Aminoalkenes 5–8, Amines 9–12, Cycloalkanones 13–16, and Alkenes 17–20

compound	$IP(n_N)$	$IP(n_O)$	$IP(\pi_{C=C})$
1-methyl-4-piperidone (**1**)	8.82	9.35	
1-methylhexahydroazocin-5-one (**2**)	8.13	8.83	
1-methyloctahydroazecin-6-one (**3**)	8.20	8.83	
tropinone (**4**)	8.64	9.22	
1-methyl-4-methylenepiperidine (**5**)	8.36		9.12
1-methyl-5-methyleneoctahydroazocine (**6**)	7.79		9.00
1-methyl-6-methylenedecahydroazecine (**7**)	8.03		8.87
8-methyl-3-methylene-8-azabicyclo[3.2.1]octane (**8**)	8.25		9.10
1-methylpiperidine (**9**)	8.35		
1-methyloctahydroazocine (**10**)	8.02		
1-methyldecahydroazecine (**11**)	7.99		
tropane (**12**)	8.21		
cyclohexanone (**13**)		9.29	
cyclooctanone (**14**)		9.28	
cyclodecanone (**15**)		9.19	
bicyclo[3.2.1]octan-3-one (**16**)		9.23	
methylenecyclohexane (**17**)			9.13
methylenecyclooctane (**18**)			8.79
methylenecyclodecane (**19**)			8.91
3-methylenebicyclo[3.2.1]octane (**20**)			9.08

Chart I



X=O	**1**	**2**	**3**	**4**
CH_2	**5**	**6**	**7**	**8**
H_2	**9**	**10**	**11**	**12**

We report here our findings that transannular interactions in medium-ring amino ketones and aminoalkenes can be investigated by photoelectron (PE) spectroscopy and that valuable information about the conformation of the molecules is obtained.

Results and Discussion

We have investigated the PE spectra of the amino ketones **1–4** and of the aminoalkenes **5–8** which are isoelectronic with **1–4**. The vertical ionization potentials of all investigated compounds are collected in Table I.[5] While the π MO of the carbonyl group of **1–4** is relatively low in energy and the corresponding ionization band is located in the unresolved region of the σ ionizations, the π ionization of the olefinic double bond in **5–8** is found in the well-resolved lower part of the spectrum (<10 eV) (Chart I).

The interaction of functional groups has been studied frequently by PE spectroscopy.[9] It has been found that the interaction of two functional groups, separated by several bonds, is composed of varying amounts of through-space and through-bond contributions.[10] Throughout this investigation the validity of Koopmans' theorem[11] is assumed.

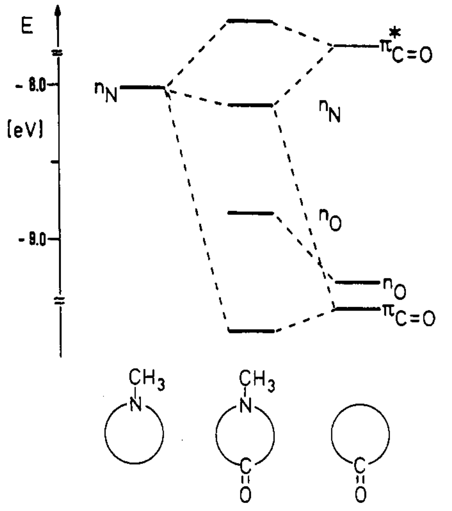
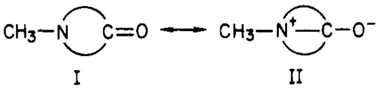


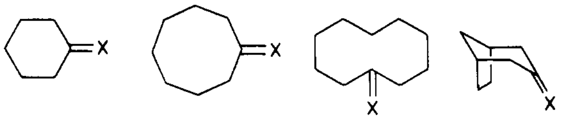
Figure 1. Qualitative interaction diagram for n and π orbitals of an amino ketone.

Chart II



(1)

Chart III



X=O	**13**	**14**	**15**	**16**
CH_2	**17**	**18**	**19**	**20**

1. **Amino Ketones.** To account for the low carbonyl reactivity and the weakened basic character of the alkaloids protopine and cryptopine, which contain an *N*-methyl and a carbonyl group in 1,6-positions of a ten-membered ring, Kermack and Robinson[12] proposed that there is electronic interaction between the functional groups.

Several cyclic amino ketones of medium ring size, including compounds **2** and **3**, have been synthesized by Leonard et al.[13] and studied by IR spectroscopy. These authors found that the carbonyl vibration has a lower frequency than usually found for cyclic ketones of the same ring size. The lowering of the carbonyl frequency by 20–30 cm^{-1} was explained by transannular amide resonance (eq 1) leading to partial single bond character of the CO bond. In accord with this interaction, protonation occurs at the oxygen atom, followed by transannular cyclization.[13] See (Chart II).

Since the energies of the n- and π-molecular orbitals of the amino and the carbonyl group should be affected and shifted due to the amount of interaction, sizable effects should be detectable in the PE spectra.

In the lower energy region (<10 eV) of the PE spectra two ionization bands are found for the amino ketones. These are attributed to the n electrons of the amino group

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[5] Pe spectra of the following compounds have been published previously: **1**,[6] **5**,[6] **9**,[6] **13**,[7] **14**,[7] **15**,[8] and **17**.[6] Except for the ketones **13–15** only minor deviations are found from the reported values. For **13–15** obviously different assignments of adiabatic and vertical transitions have been made for the n_O ionization. Vibrational splitting of this band: 1130 cm^{-1} (**13**, **14**), 970 cm^{-1} (**15**).

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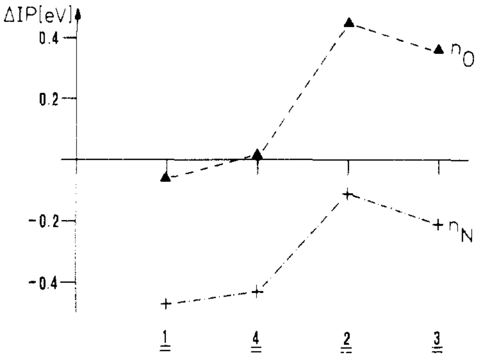

Figure 2. Shifts of IP_v values of amino ketones 1–4 relative to amines 9–12 (n_N) and ketones 13–16 (n_O).

(n_N) and the oxygen atom of the carbonyl group (n_O). It was not possible to identify the bands due to the ionization of the $\pi_{C=O}$ electrons. In Figure 1 an interaction diagram is shown for the relevant orbitals.

In order to determine the interaction of the two functional groups in 1–4 the n_N and n_O ionization potentials are compared with the respective values of the cyclic amines 9–12 and the cycloalkanones 13–16 (Chart III). For example, 1 is compared with 9 and 13. If there is no interaction between the amino and the carbonyl group, the spectrum of the amino ketone should be obtained additively from the spectra of the amine and the ketone with the same ring size. Deviations from additivity indicate interaction of the functional groups. The deviations are measured as $\Delta IP(n_N) = IP_v(\text{amine}) - IP_v(\text{amino ketone})$ and $\Delta IP(n_O) = IP_v(\text{ketone}) - IP_v(\text{amino ketone})$. Thus, negative ΔIP values indicate a stabilization of the respective orbital in the amino ketone relative to the amine or ketone, while positive ΔIP values are due to a destabilization of the MO. The ΔIP values of compounds 1–4 are summarized in Figure 2.

The data indicate small shifts of the n_O orbital in 1 and 4 but larger shifts of the same orbital in 2 and 3. The n_N orbital is shifted only slightly in 2 but to a greater extent in 1 and 4, while for 3 a medium shift is observed.

Several effects have to be considered in explaining the spectra of 1–4:[10,14] (1) Inductive effects. (2) Through-space interaction (homoconjugation) of the two chromophores, i.e., interaction of n_N and π_{CO} by direct overlap. (3) Through-bond interaction (hyperconjugation), i.e., coupling of n_N and π_{CO} with suitable σ- and σ*-bond orbitals.

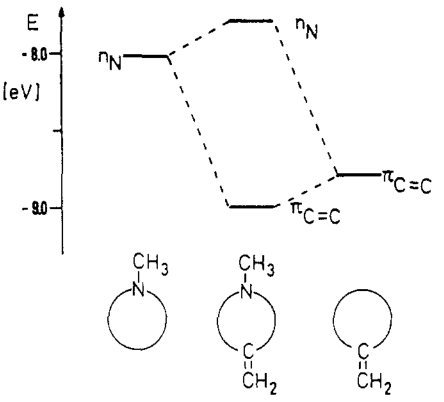

Figure 3. Qualitative interaction diagram for n and π orbitals of an aminoalkene.

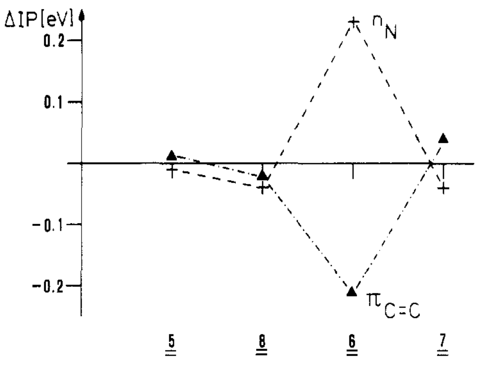

Figure 4. Shifts of IP_v values of aminoalkenes 5–8 relative to amines 9–12 (n_N) and alkenes 17–20 ($\pi_{C=C}$).

The large ΔIP values of the n_N MO in compounds 1 and 4 can be explained with inductive stabilization by the CO group. Sarneel et al,[6] who investigated the PE spectrum of 1, calculated a stabilization of 0.35 eV for the n_N orbital compared to 9 due to the substitution of the methylene group by the carbonyl group. Through-bond interaction can only play a minor part, because the nitrogen lone pair is perpendicular to the σ system. That the inductive effect of the carbonyl group is dominant in a six-membered ring was also found by Worrell et al.[15] and by Gleiter et al.[16] for azaadamantanones. Transannular interactions can be excluded as the origin of the orbital shifts in these systems, since the six-membered rings possess chair conformations with a large diametrical distance. Therefore, it is obvious that the energy of the n_N orbital cannot be considered as a suitable measure of the transannular interaction between the two functional groups in cyclic amino ketones. The same conclusion follows from the small shifts of this orbital in 2 and 3 compared with the amines 10 and 11 (Figure 2). Here the destabilization of the n_N orbital due to transannular interaction with the π_{CO} orbital is compensated by strong n_N/π^*_{CO} interactions. As has been shown by IR spectroscopy, in 2 and 3 the amino and the carbonyl group are in a close contact, while in 1 and 4 they are too far from each other.[13]

The $IP(n_O)$, on the other hand, seems to be a good indicator for transannular amide resonance in a similar way as for resonance in amides and lactams.[17] The destabilization of this orbital in 2 and 3 may be explained to result from a slight rehybridization of the oxygen atom due to the interaction of the two functional groups leading to a higher p contribution. The classical description of the transannular amide resonance is leading to the same result. Here the lower ionization energy of the n electrons is a result of the negative charge on the oxygen atom in the polar resonance formula II (Chart II) (eq 1).

2. Aminoalkenes. The aminoalkenes 5–8 are isoelectronic with the amino ketones 1–4. These compounds are much better suited for PE spectroscopy, since both interesting MO's, n_N and $\pi_{C=C}$, are easily accessible in the lower energy range of the spectrum, and the interpretation of the spectra is not complicated by large inductive effects. In addition, interactions with the π* orbital are of minor importance, since this MO is separated in energy from the n and the π orbital to a higher extent than in the amino ketones. An interaction diagram between the relevant orbitals is shown in Figure 3.

Through-space interaction will stabilize the π and destabilize the n orbital. For 5–8 the reference molecules are the cyclic amines 9–12 and the methylene alkanes 17–20.

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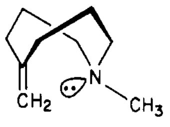
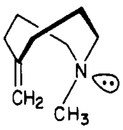
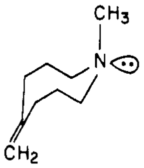
Chart IV



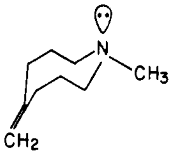
6a



6b



6c



6d

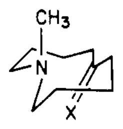
The ΔIP values, $\Delta IP(n_N) = IP_v(\text{amine}) - IP_v(\text{aminoalkene})$ and $\Delta IP(\pi_{C=C}) = IP_v(\text{alkene}) - IP_v(\text{aminoalkene})$, are summarized in Figure 4.

The data indicate that the n_N and the $\pi_{C=C}$ ionizations of **5**, **7**, and **8** are nearly unchanged compared to the respective monofunctional compounds **9** + **17**, **11** + **19**, and **12** + **20**. These findings indicate the absence of sizable interactions between the functional groups in these aminoalkenes. On the other hand, for **6** both the n_N and the $\pi_{C=C}$ ionizations deviate considerably from the respective values of the monofunctional molecules **10** and **18**, indicating strong transannular interaction between the amino group and the C=C double bond. This result may be attributed to conformation **6a**, which in contrast to **6b**, **6c**, and **6d** has a close contact between the two chromophores. Conformations **6a**–**d** have been drawn in analogy to the boat-boat and boat-chair forms of cyclooctane and heterocyclic analogues.[18] The well-known property of a saturated eight-membered ring to favor this type of interaction has been demonstrated—to our knowledge—for the first time for an aminoalkene. See Chart IV.

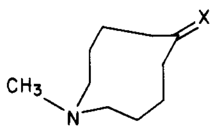
The IR spectrum of **6** gives an additional clue for the transannular interaction in this molecule. While the C=C stretching vibration is located between 1640 and 1650 cm^{-1} in **5**, **7**, and **8**, a value of 1625 cm^{-1} is found for **6**. The lower frequency indicates a weaker C=C bond in **6** due to the interaction with the amino group.

According to these findings compound **6** shows a similar behavior as the isoelectronic amino ketone **2**: in both systems with an eight-membered ring there is strong transannular interaction. On the other hand, the compounds with a ten-membered ring deviate from each other: while in the amino ketone **3** there is sizable resonance, this is negligible in the aminoalkene **7**. This might be due to different conformational properties of **3** and **7**. While for **3** a conformation like **3a** with a close contact between the functional groups is most probable, **7** should prefer a form like **7b** with a great separation of the nitrogen lone-pair electrons and the C=C double bond. The stabilization of **7b** relative to **7a** is at least in part caused by the smaller dipole moment of the former conformation. In addition, it may reflect the higher electrophility of the carbonyl group compared to the olefinic double bond. See Chart V.

Chart V



X=O **3a**
X=CH2 **7a**



3b
7b

Conclusion

By comparison with the results of other methods[13] it has been established that for amino ketones the ionization potential of the n_O electrons can be considered as an indicator for transannular interactions between amino and carbonyl group. This result is analogous to the findings for the resonance in amides and lactams.[15] The energy of the n_N orbital is susceptible to various effects of the carbonyl group: inductive stabilization, destabilization through n_N/π_{CO} interaction, and stabilization through n_N/π^*_{CO} interaction. Therefore, it is difficult to determine the contribution of transannular interaction.

For aminoalkenes the shifts of the n_N and the π_{CC} MO's relative to the respective values of the monofunctional compounds directly indicate the amount of n/π interaction. Further investigations are necessary to analyze the relative contribution of through-space and through-bond interactions and their dependence on ring size and conformation.[19,20] The question, whether the transannular interactions are reflected in the chemical properties of these compounds,[21] will also be investigated.

Experimental Section

The PE spectra have been recorded in the region of 6–21 eV on a UPG 200 spectrometer of Leybold-Heraeus with He I excitation (21.21 eV). The calibration of the energy scale was performed with an Ar-Xe mixture. The accuracy of the measurement was ±0.02 eV for ionization potentials. ^{1}H NMR spectra were run on a Hitachi/Perkin-Elmer R24 spectrometer, and ^{13}C NMR spectra were run on a Varian XL-200 spectrometer with tetramethylsilane as internal standard. For IR spectra a Perkin-Elmer 397 was used; for mass spectra a Finnigan MAT312 (72 eV) was used. Elemental analyses were carried out on a Heraeus EA301 C, H, N analyzer.

Compounds **1**, **4**, **9**, **13**, **14**, **15**, and **17** have been obtained from Aldrich. Substances **2** and **3** have been synthesized by the method of Leonard et al.[13] The amines **10**, **11**, and **12** have been synthesized from the corresponding amino ketones by Huang-Minlon reduction.[13] The alkenes **5**, **6**, **7**, **8**, **18**, **19**, and **20** have been synthesized from the corresponding ketones by Wittig reaction.[22] The procedure is described for **6** and **8**, which have been prepared for the first time. The purity of all compounds was checked by analytical GC.

1-Methyl-5-methyleneoctahydroazocine (6). The Wittig reaction was executed in an argon atmosphere. A solution of 7.57 g (21.2 mmol) of methyltriphenylphosphonium bromide and 2.38 g (21.2 mmol) of potassium *tert*-butanolate in 150 mL of dry THF was stirred for 15 h. To this mixture were added 3.00 g (21.2 mmol) of **2**, and stirring was continued for an additional 15 h. Then the solid was removed by filtration, the filtrate was evaporated under reduced pressure, and the residue was purified by vacuum distillation (82 °C/20 mm). Further purification was achieved by preparative GC: Chromosorb PNAW 60, 10% CW 20M + 2% KOH (column length 1.8 m, 140 °C); yield 1.69 g (57.1%); IR (liq) ν 2760 (NCH_3), 1625 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 4.65 (s, 2 H, C=CH_2), 2.65–1.95 (m, 8 H, CH_2), 2.28 (s, 3 H, NCH_3), 1.90–1.40 (m, 4 H, CH_2); ^{13}C NMR (C_6D_6) δ 152.2 (s), 110.2 (t), 55.6 (t), 46.0 (q), 35.1 (t), 29.7 (t); MS, *m/e* 139 (M^+).

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Anal. Calcd for $C_9H_{17}N$: C, 77.63; H, 12.21; N, 10.06. Found: C, 77.95; H, 12.44; N, 9.96.

8-Methyl-3-methylene-8-azabicyclo[3.2.1]octane (8). The same procedure was applied as described for **6**: bp 58 °C/15 mm; yield 40.3%; IR (liq) ν 2800 (NCH_3), 1650 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 4.65 (s, 2 H, $C{=}CH_2$), 3.05 (m, 2 H, CH), 2.70–1.00 (m, 8 H, CH_2), 2.30 (s, 3 H, NCH_3); MS, *m/e* 137 (M^+).

Anal. Calcd for $C_9H_{15}N$: C, 78.77; H, 11.02; N, 10.21. Found: C, 78.70; H, 11.41; N, 10.11.

Acknowledgment. We are indebted to Mr. R. Poppek for excellent assistance with the recording of the PE spectra.

Registry No. **1**, 1445-73-4; **2**, 71512-38-4; **3**, 19641-26-0; **4**, 532-24-1; **5**, 13669-28-8; **6**, 99838-32-1; **7**, 57839-84-6; **8**, 99838-33-2; **9**, 626-67-5; **10**, 19719-81-4; **11**, 6480-47-3; **12**, 529-17-9; **13**, 108-94-1; **14**, 502-49-8; **15**, 1502-06-3; **16**, 14252-05-2; **17**, 1192-37-6; **18**, 3618-18-6; **19**, 3817-57-0; **20**, 4877-39-8; $MePh_3P^+Br^-$, 1779-49-3.

Assignments of the Carbon Resonances in *tert*-Butylated 2-Naphthols by the Two-Dimensional C-Relayed H,C-COSY Technique

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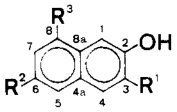
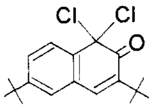
The signals of the aromatic carbon atoms in three *tert*-butylated 2-naphthols were assigned by the new two-dimensional NMR technique C-relayed H,C-COSY. The application of only one-bond coupling constants avoids any ambiguities in the assignment. A number of previous assignments had to be changed. The chemical shift values and one-bond C–C coupling constants have been correlated with electron densities and bond orders, respectively.

The elucidation of molecular constitution by NMR spectroscopy is equivalent to an unambiguous assignment of NMR signals to distinct atoms. Reliable assignments are the basis of the discussion of substituent effects on chemical shifts, of the investigation of biosynthesis by isotope substitution, and of the discussion of the stereostructure derived from NMR parameters. Information on the connectivity of atoms (constitution) is provided by scalar coupling (through-bond coupling, *J* coupling). In cases where an unequivocal assignment of the NMR signals is required, we strongly recommend to start the NMR spectroscopic analysis, as far as possible, by using *J* couplings for assignments. As an example, we demonstrate the application of this approach to the aromatic carbon signals of the mono-, di-, and tri-*tert*-butylated 2-naphthols **2**–**4**.



	R^1	R^2	R^3
1	H	H	H
2	H	t-Bu	H
3	t-Bu	t-Bu	H
4	t-Bu	t-Bu	t-Bu



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The reason for the choice of these compounds was a controversy over the structure of the (di-*tert*-butylation products of 2-naphthol (**1**),[2–5] which has lasted for decades, as well as a discrepancy about the structure of their chlorination products,[6–8] and about the reaction conditions for their selective preparation.[9,10]

The structures of the mono-, di-, and tri-*tert*-butyl-2-naphthols obtained on *tert*-butylation of **1** are now accepted to be **2**, **3**, and **4**, respectively,[4,5,10] and the structure of the dichlorination product of **3** turned out to be **5**.[7,8] Moreover, it is claimed[10] that at temperatures of <90 °C **4** is formed, whereas temperatures of >90 °C lead to **3** (if **1** is alkylated by isobutene). On the other hand, there is still disagreement in assigning the ^{13}C NMR resonances of the ring carbons of **3**,[5,10] on the basis of shift arguments and CH couplings (one-dimensional spectra). Furthermore, since Chasar[10] assigned long-range CH couplings in terms of $^2J > 0$ and $^3J \sim 0$, contrary to the usual rules ($^2J \sim 0$ and $^3J > 0$) for aromatic carbons,[11] an unambiguous assignment of the signals of the ring carbon atoms of **2**–**4** which does not rely on long-range couplings is highly desirable.

Results and Discussion

A maximum of three two-dimensional NMR techniques (2D NMR) was necessary: H,H-COSY[12] for the elucidation of proton couplings across three or four bonds, H,C-COSY for heteronuclear one-bond couplings $^1J_{CH}$,[13–15] and C-re-

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