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

Horst Kessler,* Wolfgang Bermel,[1] and Christian Griesinger

Institute of Organic Chemistry, J.W. Goethe-University, D-6000 Frankfurt 50, West Germany

Peter Hertl, Edgar Streich, and Anton Rieker*

Institute of Organic Chemistry, Eberhard-Karls-University, D-7400 Tübingen 1, West Germany

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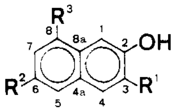
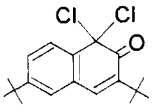
The signals of the aromatic carbon atoms in three *tert*-butylated 2-naphthols were assigned by the new two-dimensional NMR technique C-relayed H,C-COSY. The application of only one-bond coupling constants avoids any ambiguities in the assignment. A number of previous assignments had to be changed. The 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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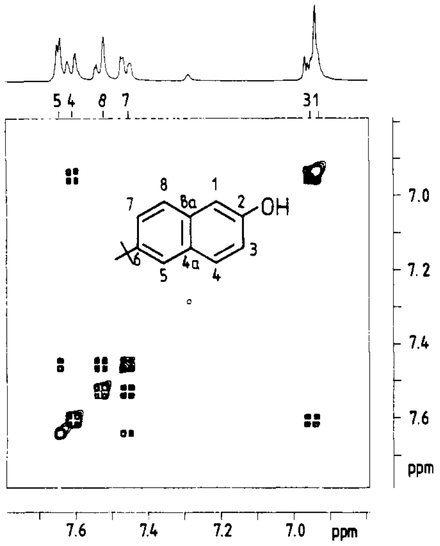

Figure 1. H,H-COSY spectrum of **2** (for measuring conditions, see Experimental Section).

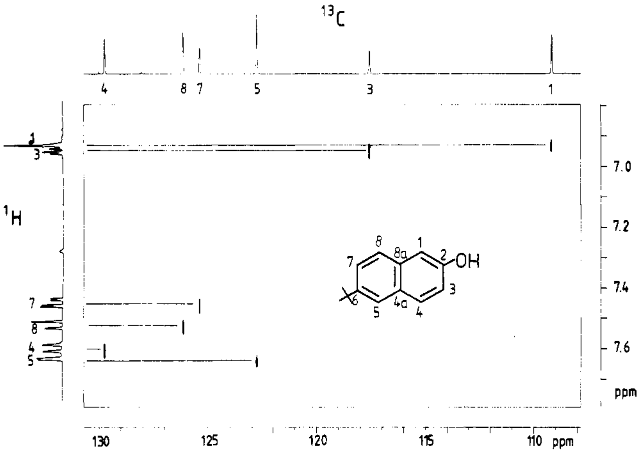

Figure 2. H,C-COSY spectrum of **2** (for measuring conditions, see Experimental Section)

layed H,C-COSY for a combined use of $^1J_{CH}$ and $^1J_{CC}$.[16] Since all techniques begin with a "proton labeling" in t_1, showing the normal proton spectrum in the F_1 domain, we chose solvent mixtures ($CDCl_3/C_6D_6$) in which the proton signals are separated. Identification of the proton spin systems for the three compounds **2**–**4** was straightforward.

As an example the H,H-COSY spectrum of **2** is shown in Figure 1. The signal at lowest field (7.65 ppm) exhibits a small coupling (meta coupling) to the signal at 7.46 ppm, which is coupled to the signal at 7.53 ppm (ortho coupling). The mutual coupling is identified by the off-diagonal signals (the so-called cross peaks) in the two-dimensional spectrum. The spin system of the other ring is identified in the same manner. The small chemical shift difference between H-1 and H-3 makes the identification of their mutual coupling impossible from this spectrum, but the C-relayed H,C-COSY spectrum (Figure 4, see below) proves also the 1,3-connectivity by the appearance of couplings to the quaternary carbon 2. In addition, the high-field shift of both protons (H-1 and H-3) is typical for protons in ortho position to the hydroxyl group.

The carbons connected to the aromatic protons are assigned via an H,C-COSY spectrum without any ambiguity in the usual manner (Figure 2).

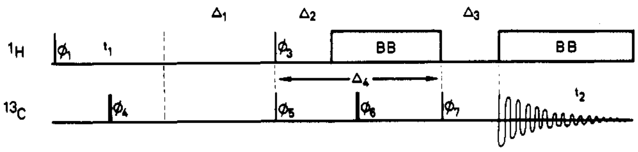

Figure 3. Pulse sequence for the C-relayed H,C-COSY technique.

The spectra shown in Figures 1 and 2 are only compatible with the structures having the *tert*-butyl group in position 6 or 7. The discrimination between them requires an information from one benzene ring to the other. Although this could be achieved by NOE effects, we use in this paper heteronuclear couplings which by the same token assign the quaternary carbon signals. Two general strategies exist for the assignment of quaternary carbons: *Heteronuclear long-range couplings* across two, three, and, in rare cases, four bonds are exploited in the H,C-COLOC experiment.[17] Based on the well-agreed-upon assumption of $^3J_{CH} \approx 6$–8 Hz and $^2J_{CH} \leq 2$ Hz in each aromatic system,[11] the COLOC technique would in this case provide the assignment of all quaternary carbons. However, COLOC could not be applied here in order to obtain an assignment of the quaternary carbons independent of the magnitude of heteronuclear long-range couplings and thus resolve the controversy in the literature.[5,10] We therefore decided to use a second strategy based only on *one-bond couplings* for the assignment in the naphthols **2**–**4**. Despite the inherent sensitivity loss of more than one magnitude due to the low abundance of pairs of connected ^{13}C nuclei, the use of $^1J_{CC}$ couplings normally[18] gives unequivocal information on the carbon connectivity. 2D-INADEQUATE is the appropriate technique for this approach.[19] In order to enhance the poor sensitivity, polarization transfer from proton to carbon via $^1J_{CH}$ couplings was introduced some years ago in the INEPT-INADEQUATE experiment.[20] Recently some of us have described the 1D and 2D version of the C-relayed H,C-COSY,[16] which achieves an additional sensitivity enhancement of up to a factor of 2. We will show here that the latter technique can be applied to obtain unambiguous assignments of quaternary carbons and by this way the complete connectivity.

The pulse sequence (Figure 3) works in the following way for a $H_n{}^{13}C$-$^{13}C^q$ fragment: proton magnetization, labeled with the characteristic chemical shifts during the evolution period t_1 is transferred via $^1J_{CH}$ to the directly bonded carbon, CH_n. $^1J_{CH}$ coupling is optimally refocused in the delay Δ_2 before switching on the decoupler. $^1J_{CC}$ coupling evolves during the delay Δ_4, and carbon magnetization is finally transferred to the quaternary carbon C^q. Strong signals of nonquaternary carbons can be suppressed to some extent by switching off the decoupler during $\Delta_3 = (2J_{CH})^{-1}$ prior to acquisition.[21] Phase cycling as described in ref 16 is applied.

The C-relayed H,C-COSY spectrum of the four quaternary aromatic carbons of the mono-*tert*-butyl-2-naphthol **2** is shown in Figure 4. The vertical axis (F_1) contains the proton spectrum, the horizontal axis the

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Table I. Carbon Chemical Shifts[a,b] and Carbon–Carbon Coupling Constants in *tert*-Butylated 2-Naphthols

	δ			J, Hz			
C	2[c]	3[d]	4[e]	bond	2	3	4
1	109.17	110.51	110.92	1–2	71.9	69.9	71.0
2	152.87	153.15	151.39	2–3	62.4		
3	117.54	138.39	136.64	3–4		64.0	63.5
4	129.72	126.17*	127.54*	4–4a	*f*	56.1	56.1
4a	128.90	129.13	130.54*	4a–5	57.0	57.1	57.3
5	122.73	123.09*	122.13*	5–6	62.4	63.0	62.3
6	146.18	146.18	144.95	6–7	54.3	55.1	54.8
7	125.35*	124.84*	122.01*	7–8			63.5
8	126.11*	125.14*	143.03	8–8a	55.6	56.1	
8a	132.72	131.40	128.96*	8a–1	59.7	59.1	58.5

[a] Quaternary carbons were assigned by C-relayed H,C-COSY and tertiary carbons (CH) by H,C-COSY. The ^{1}H NMR spectrum of 2 was analyzed by H,H-COSY. [b] The assignments marked by asterisks are at variance with those given in ref 10. [c] Solvent: $CDCl_3/C_6D_6$ (5:1). [d] Solvent: $CDCl_3/C_6D_6$ (2:1). The values obtained in $CDCl_3$ solution are: 110.31, 152.91, 138.25, 125.95, 128.80, 122.77, 146.15, 124.71, 124.91, 131.05 [in the order of carbon atoms]. [e] Solvent: $CDCl_3$. [f] Cross peak not detected.

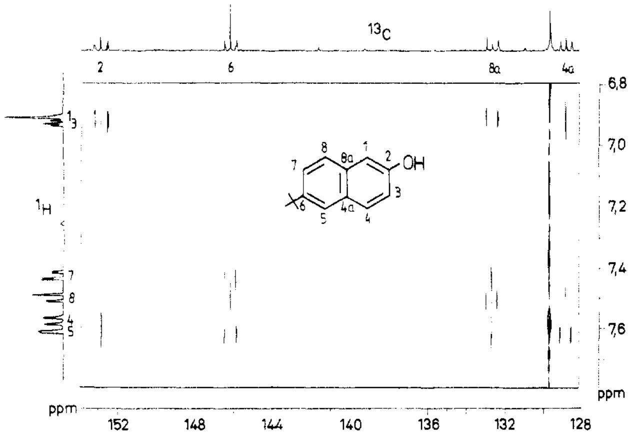

Figure 4. C-Relayed H,C-COSY spectrum of 2 (for measuring conditions, see Experimental Section).

projection of the carbon 2D spectrum. Every "relayed peak" is characterized by the splitting due to carbon–carbon coupling. Additional signals (so-called "COLOC peaks"), not split in the carbon dimension, are caused by proton–carbon long-range couplings. These long-range couplings also evolve during Δ_1 and Δ_2, but polarization transfer occurs only to a small extent, because both delays are optimized for the evolution of $^1J_{CH}$ which are about 10 times larger than $^nJ_{CH}$ ($n > 1$). Nevertheless, since all molecules containing the fragment $H^{12}C–^{13}C^q$ (abundance 10^{-2}) contribute to these COLOC peaks, even an excitation of about 1% yields signals of similar intensity as that of the relayed peaks which originate from molecules with a $H^{13}C–^{13}C^q$ fragment (abundance 10^{-4}).

The two structural possibilities (*tert*-butyl group in 6- or 7-position) which remain after the discussion of the H,H-COSY and the H,C-COSY spectra (see above) can be distinguished in the C-relayed spectrum: the already assigned protons H-1 and H-3 excite C-2; H-1 also excites another carbon which therefore has to be C-8a. The other relayed peak of C-8a leads to the assignment of H-8, whose J_{HH} coupling pattern allows the identification of H-7. The signal at 146.18 ppm, which shows a relayed peak to H-7, is easily assigned to C-6, thus also providing the assignment of H-5. This assignment is independently proven by the $^4J_{HH}$ coupling between H-7 and H-5 (7.62 ppm). The assignment of H-5 finally leads to the identification of C-4a. Although a cross peak at C-4a from H-4 is missing (most probably due to strong coupling between C-4 and C-4a) there is no doubt that 2 is 6-*tert*-butyl-2-naphthol.

Additionally, C-relayed H,C-COSY spectra yield the carbon–carbon coupling constants in the fragment $H_nC–C^q$ as well as the identification of the coupling partners. Their values are compiled in Table I, together with chemical shift values of the aromatic carbons.

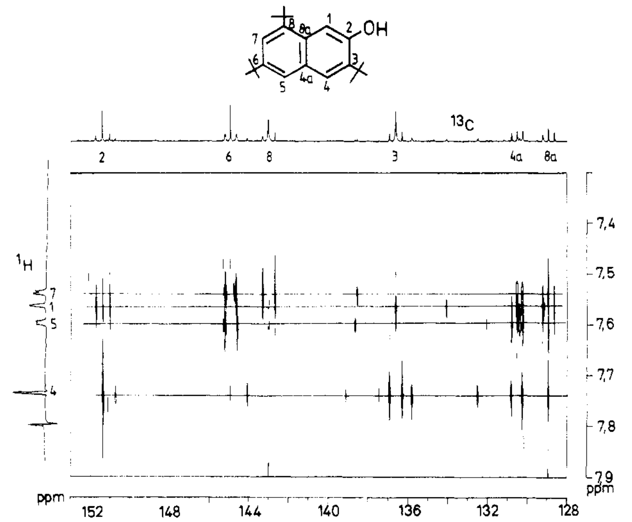

Figure 5. C-relayed H,C-COSY spectrum of 4 (for measuring conditions, see Experimental Section).

The structures of 3 and 4 are solved in the same way. As an example the C-relayed H,C-COSY of 4 is presented in Figure 5. The proton spectrum shows an AM system (1,3 coupling) and two singlets (protons in 1,4-positions). Some long-range coupling is indicated by broadening of the signals at 7.56 and 7.59 ppm. We begin the evaluation of the spectrum with the signal of C-2, shifted downfield by the hydroxy group. The C-relayed peak to the singlet at 7.56 ppm assigns this to H-1, which also excites C-8a. The other singlet therefore corresponds to H-4 (1,4-positions). The C-relayed peak at this resonance defines the two adjacent carbons (C-3 and C-4a). Only C-4a is excited from another proton (H-5). Continuing with H-5, carbon 6 is assigned, which also yields a cross peak to H-7. The assignment of C-8 via H-7 closes the cycle.

The intensity of COLOC peaks (center peaks) in the projection spectrum for carbons 6, 8, and 3 is higher than one would expect from the 2D plot shown in Figure 5. These intense peaks result from couplings to the methyl protons of the *tert*-butyl groups which can be seen in the full 2D plot. They can be used to assign the *tert*-butyl groups (without using comparison of chemical shift values in different compounds!).

The chemical shift values in Table I exhibit some differences compared to those reported in the literature. Thus, in our earlier paper[5] the assignment of C-4 and C-8 of 3 must be interchanged, whereas 11 of Chasar's[10] assignments for 2–4 (marked by asterisks in Table I) turned out to be incorrect. Eight of them had already been classified as interchangeable;[10] however, the proposed exchange partners proved to be correct only in one case (C-7/C-8 of **2**). Two more assignments, indicated as exchangeable (i.e., C-4/C-5 of **2**) could be verified.

We will now discuss the results of Table I and the possible reasons for the above-mentioned differences from the literature data in terms of chemical shifts and long-range C–H and one-bond C–C couplings.

^{13}C Chemical Shifts. The chemical shift of a ring carbon atom in alternant polycyclic aromatic hydrocarbons like naphthalene is in principle dependent on the π-electron density q^π, the σ-electron density q^σ, and the sum of the mobile bond orders P (eq 1),[22] benzene being the reference compound.[23] Furthermore, it was suggested that

$$\Delta\delta_C = 100\Delta q^\pi + 67\Delta q^\sigma - 76\Delta P \qquad (1)$$

δ_C was governed primarily by the π-electron density at each carbon.[11] In order to scrutinize the effect of multiple *tert*-butyl substitution on these facts, we calculated the π-electron densities q^π of **1**–**4** by CNDO/2.[24,25] A correlation of these values with the ^{13}C chemical shifts of the respective ring-carbons of **1** (taken from ref 11) and **2**–**4** (Table I) yields a linear dependence with correlation coefficients of 0.90, 0.92, 0.84, and 0.84, respectively. The use of INDO for the calculations did not improve the correlation noticeably. For all compounds **1**–**4**, correlation of $\delta_{^{13}C}$ vs. q^π(HMO) is worse than correlation vs. q^π(CNDO). Furthermore, correlation of $\delta_{^{13}C}$ vs. $q^{\pi+\sigma}$ (valence electron density, calculated by CNDO) is of the same quality (r = 0.90, 0.86, and 0.87 for **2**, **3**, and **4**, respectively). The reason is that q^σ generally changes to a lesser degree than q^π in moving from one carbon to the other.[26] Naturally, the invariance of q^σ is highest, when no substituent is present; hence, in the case of **1** itself, r = 0.98. On the other hand, Wilson and Stothers[27] have found a somewhat poorer correlation[28] of $q^{\pi+\sigma}$ vs. δ_C for alkyl naphthalenes.

Having unequivocally assigned all ^{13}C NMR signals of **2**–**4**, we were interested in a possible simple additivity of the substituent-induced shift (SIS) contributions to δ_C. If we add the SIS values of a *tert*-butyl group (derived by subtraction of the δ_C values of naphthalene[11] from those of 2-*tert*-butylnaphthalene[29] to the corresponding δ_C values of 2-naphthol,[11] we can calculate δ_C values for **2**, which deviate from those of Table I only to a degree of ±0.03–0.39 ppm, as expected.[30] Similarly, the chemical shifts for **3** were calculated by starting either with the experimental values of **2** (by using the SIS contributions of another β-*tert*-butyl group[29]) or with those of 2,7-di-*tert*-butylnaphthalene[29] by using the SIS contribution of a β-hydroxy group, obtained by subtraction of the ^{13}C chemical shift values of naphthalene[11] from those of 2-naphthol[29]). This procedure led to larger deviations from the experimental values (Table I) (±0.02–1.94 ppm and ±0.02–2.15 ppm, respectively), the signals of C-1 to C-4 revealing the highest discrepancies. Nonadditivity of SIS contributions in the case of 1,2-disubstitution has already been observed and discussed for other naphthalene derivatives.[27] Finally, calculating the shift values for **4** from the experimental values of **3** and the SIS contribution of an α-*tert*-butyl group (obtained by subtraction of the chemical shifts of naphthalene from those of 1-*tert*-butylnaphthalene[29]) yielded again close agreement with the experimental data (±0.01–0.62 ppm), with the sole exception of $\delta_{C\text{-}1}$ (−1.56 ppm). The lower experimental value probably reflects the steric effect of the 8-*tert*-butyl group on the C-1–H fragment (periinteraction).[29]

Long-Range C–H Couplings. From the assignments of the ^{13}C signals of **2**–**4** and the corresponding [^{13}C, ^{1}H] coupled spectra, it is clearly evident, that $^3J_{C,H} > {}^2J_{C,H}$ is valid also for the naphthalene system. This fact was underlying our earlier assignments for **3**;[5] unfortunately, however, C-4 and C-8 are both ^3J coupled to *one* proton in the annelated ring, i.e., H-5 and H-1, respectively. The coupling constants of 4.6 and 3.4 Hz did not allow a discrimination, especially since values for comparison were not at hand. The unequivocal assignment of C-4 and C-8 in this work yields the correct correlation, i.e., $^3J_{C\text{-}4,H\text{-}5}$ = 4.6 Hz, $^3J_{C\text{-}8,H\text{-}1}$ = 3.4 Hz.[38]

Although Chasar[10] invariably used $^2J_{CH} > {}^3J_{CH}$ for the assignment of the carbon atoms in **2**–**4**, only those shift values as indicated by asterisks in Table I were incorrectly assigned. The reason is that several carbon atoms would show the same splitting pattern, irrespective of whether $^2J_{CH}$ or $^3J_{CH}$ is the relevant coupling (e.g., **2**, C-3,C-4,C-7,C-8; **3**; C-2,C-3,C-4a,C-7,C-8; **4**, C-1,C-2,C-3,C-8).

Furthermore, Chasar assigned C-4a and C-8a both by their relative constancy (of chemical shift) among **1**–**4**. This led to a reversed order of C-4a and C-8a in **4**, because the influence of the *tert*-butyl group in position 8 was not considered. The splitting pattern of C-8a in the totally proton-coupled ^{13}C NMR spectrum of **3** was described as an "AB quartet" due to ^2J coupling to (nonequivalent) H-1 and H-8. In reality, it is a genuine quartet, resulting from the three nearly equivalent ^3J couplings to H-4, H-5, and H-7.

One-Bond C–C Couplings. The J values of Table I obtained for **2**–**4** are in the expected range and show about the same gradation in size, as has been found for other 2-naphthalene derivatives[11,31] with the important exception of $^1J_{1,2}$ and $^1J_{2,3}$, which are ca. 8–10 Hz larger than expected. This effect has to be ascribed to the 2-hydroxy group, as has already been reported for phenol,[32] 1-naphthol,[33] and 1-phenanthrol.[34] The substituent effect of the *tert*-butyl groups on the coupling constants is noticeable only for $^1J_{1,2}$ and $^1J_{8a,1}$, as far as **2**–**4** are compared among themselves. Obviously, it is small, and its discussion not straightforward.

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[23] For more details, see; e.g.: Kalinowski, H.-O.; Berger, S.; Braun, S. "^{13}C-NMR-Spektroskopie"; Georg Thieme Verlag: Stuttgart, 1984; Chapter 3, p 88.

[24] Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

[25] (a) Several CNDO, INDO, or MINDO calculations of 2-naphthol have been reported; however, q^π and $q^{\pi+\sigma}$ values were not given explicitely.[25b] (b) See, e.g.: Rosenberg, J. L.; Brinn, I. M. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 448. Takai, H.; Odani, A.; Sasaki, Y. *Chem. Pharm. Bull.* **1979**, *27*, 1780.

[26] This conclusion is confirmed by the results of a two-parameter correlation ($\delta_C = aq^\pi + bq^\sigma + c$) analyzing the σ- and π-density effects on the ^{13}C chemical shift separately. We found that a (contribution of the π-electron density) is ca. 2–3 times larger than b (contribution of the σ-electron density), indicating δ_C to be more sensitive toward variations of the π-electron density. Since a simple linear relationship δ_C vs. $q^{\pi+\sigma}$ does not distinguish between the two different contributions, the quality of the regression increased by using the two-parameter correlation (r = 0.94, 0.90, and 0.92 for **2**, **3**, and **4**, respectively).

[27] Wilson, N. K.; Stothers, J. B. *J. Magn. Reson.* **1974**, *15*, 31.

[28] The correlation coefficient r for 2-methylnaphthalene, calculated by us from the shift values and the total charges q of ref 27 (taken from Table I and Figure 2, respectively) amounts to ca. 0.80.

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[30] As a consequence, the assignments for C-1 and C-3 of 2-*tert*-butyl-naphthalene, given in ref 11, must be exchanged.

[31] Berger, S. *Org. Magn. Reson.* **1984**, *22*, 47.

[32] Stöcker, M. *Monatsh. Chem.* **1982**, *113*, 1415.

[33] Hansen, P. E.; Poulsen, O. K.; Berg. A. *Org. Magn. Reson.* **1975**, *7*, 475.

[34] Berger, S.; Zeller, K. P. *Org. Magn. Reson.* **1978**, *11*, 303.

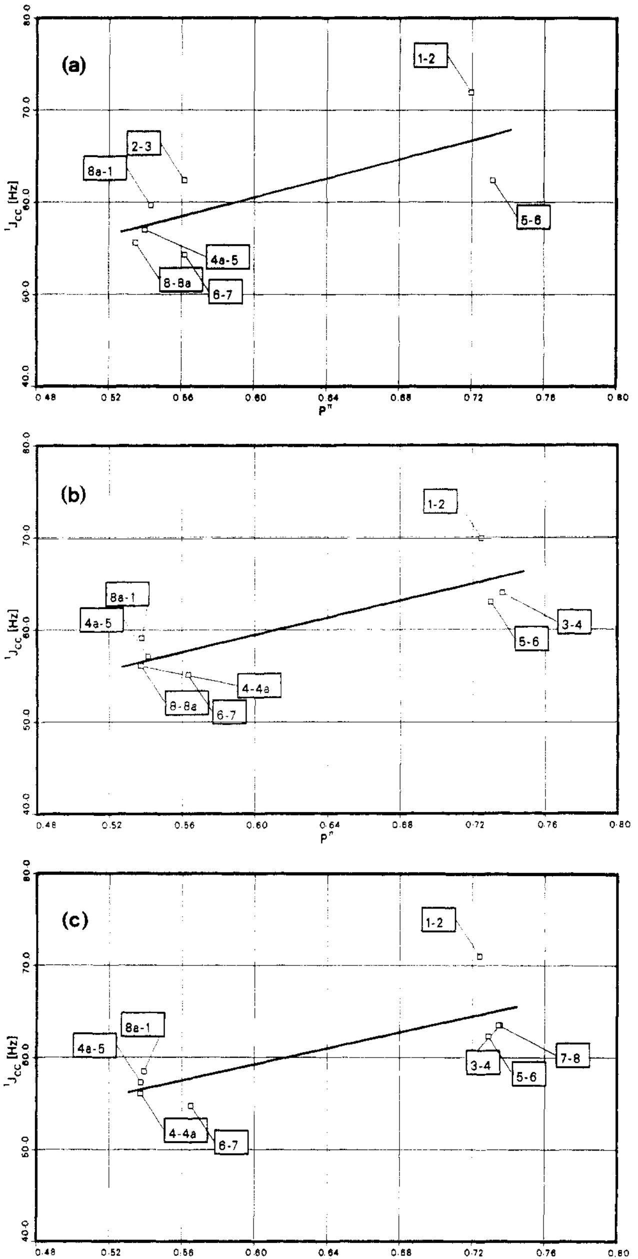

Figure 6. Correlation of $^1J_{CC}$ vs. P^π: (a) **2**; (b) **3**; (c) **4** [see text].

According to the theory of Ramsey and Purcell,[35] the electron-mediated coupling between two nuclear spins in a molecule is given by eq 2 (J^{FC}, the "Fermi contact term,

$$J = J^{FC} + J^{OD} + J^{DD} \tag{2}$$

i.e., the interaction between the nucleus and the electron spin at the nuclear locus; J^{OD} the "orbital term", i.e., the interaction of the nuclear magnetic moment and the orbital momentum of the electron; J^{DD}, the "dipole term", i.e., the dipolar interaction of the magnetic moments of nucleus and electron). There is no general agreement as to the contributions of the individual terms. For $^1J_{CC}$ in carbon–carbon single bonds a correlation to the % s character of the orbitals holds, indicating that those couplings are dominated by J^{FC}. For multiple bonds the other contributions (J^{OD} and J^{DD}) and π-electron densities also have to be considered. Nevertheless, it is somewhat surprising that for aromatic systems a linear correlation of $^nJ_{CC}$ vs. π-bond orders (P^π) is found.[11,31,34,37] Especially, 1- and 2-methylnaphthalenes reveal a good correlation ($r = 0.9689$ for 22 values) of $^1J_{CC}$ vs. P^π, as obtained from a HMO treatment.[31] Therefore, we were interested in whether such a relationship also holds in the case of **2–4**. The results are shown in Figure 6a–c. In all three cases, undoubtedly, there *is* a linear correlation of $^1J_{CC}$ vs. P^π (CNDO). The slopes of all three plots (δ/P^π) are the same, within the limit of error (47 Hz/π-bond). The axis intercepts for $P^\pi = 0$ also lie close together (ca. 31 Hz). However, the correlation coefficients r (0.75, 0.88, and 0.83, respectively) are not satisfactory. They are even worse for plotting $^1J_{CC}$ vs. P^π (HMO), the method that was used by Berger.[31]

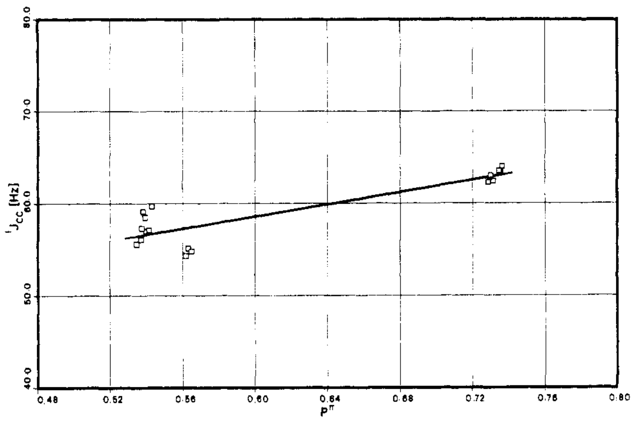

Figure 7. Correlation of $^1J_{CC}$ vs. P^π for **2–4**, $^1J_{1,2}$ and $^1J_{2,3}$ excluded [see text].

How can we understand these discrepancies? A closer inspection of Figure 6a–c reveals that in all three correlations the values for $J_{1,2}$ (and for $J_{2,3}$ of **2**) deviate most from the straight line. At the same time, these two coupling constants are much larger than expected for a 2-substituent (as compared to 2-H or 2-Me) (vide supra). Indeed, if we plot $^1J_{CC}$ vs. P^π(CNDO) without using $^1J_{1,2}$ and $^1J_{2,3}$, the correlations become also better for **3** and **4** with $r = 0.90$ and 0.93, respectively. (In the case of **2** such a correlation is nonsensical because of too few data points). Figure 7 shows the correlation of all $^1J_{CC}$ for **2–4** with the exclusion of $^1J_{1,2}$ and $^1J_{2,3}$ values (19 points), with $r = 0.89$ ($\pi/P^\pi = 33.0$ Hz/π-bond; axis intercept = 38.8 Hz). If the latter are included, r drops to 0.81 ($\pi/P^\pi = 45.5$ Hz/π-bond; axis intercept = 32.4 Hz). As a consequence, we may conclude that the observation of Berger[31] for methylnaphthalenes ("weak substituents") should not be generalized. Obviously, the effect of "strong" substituents, as for instance hydroxy, on $^1J_{CC}$ across adjacent bonds is only partially determined by their π-bond orders.

Conclusion

With three 2D NMR techniques (H,H-COSY, H,C-COSY, C-relayed H,C-COSY), the ^{13}C chemical shifts of three *tert*-butylated 2-naphthols (**2–4**) were assigned unambiguously. As a consequence, wrong assignments in the literature[5,10] could be corrected and the substitution pattern of these naphthols proved finally by a direct method. Furthermore, it was shown that Chasar's assumptions[10] on the magnitude of $^3J_{CH}$ relative to $^2J_{CH}$ are not true. Also it turned out that in the case of ortho or peri disubstitution the additivity of SIS values is not generally valid, which may lead to wrong assignments of carbon signals.

Without additional effort, most of the $^1J_{CC}$ constants of **2–4** could be determined from natural abundance. The advantage of the applied technique compared to a 2D

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(35) For details, see ref 23, chapter 4, p 420, and ref 36.

(36) Krishnamurthy, V. V.; Prakash, S. G. K.; Iyer, P. S.; Olah, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 7068.

(37) Hansen, P. E.; Poulsen, O. K.; Berg, A. *Org. Magn. Reson.* **1979**, *12*, 43.

(38) **Note added in proof**: The assignment of these coupling constants was proven by an H_1C-COLOC spectrum.

INEPT-INADEQUATE experiment[20] is that the intensity of the signals is doubled[16] in favorable cases. This can be of vital importance when the substance has low solubility or when only a limited amount is available. On the other hand, C-relayed H,C-COSY requires a resolution of the proton spin system for their "labeling" in t_1 and is restricted to the application to quaternary carbons. Similar to the 2D INEPT-INADEQUATE the dependence from the shorter relaxation times of protons is advantageous to a conventional 2D INADEQUATE technique, because the repetition rate can be higher. The so called COLOC peaks, which are caused by proton–carbon long-range couplings, appear in the spectrum as well. Those signals are easy to identify, because they are not split in the carbon dimension. They can be used as additional help for the assignment, e.g., in aromatic rings, since here $^3J_{CH}$ couplings are relatively large compared to others (vide supra). Thus, the C-relayed H,C-COSY spectrum contains also the information of a COLOC spectrum.

Correlations of δ_C vs. q^π(CNDO) and of $^1J_{CC}$ vs. P^π-(CNDO) show that π-conjugation dominates these experimental parameters as in other aromatic systems. However, the r factors for the latter correlation are not so satifactory as, e.g., in the case of 1- and 2-methylnaphthalene.[31] This reflects the effect of the hydroxy group which seems to influence $^1J_{CC}$ coupling across the adjacent C–C bonds by mechanisms different from those operating on their π-bond orders. Unless a whole series of napthalene derivatives have been measured and a more clear-cut insight into the mode of action of the substituents is obtained, generalizations should, however, be avoided.

Finally, repeating of the synthesis of **4** under conditions similar to those given by Chasar[10] (for details, see Experimental Section) revealed that lowering the temperature of *tert*-butylation to 80 °C leads to a selective formation of **4** over **3** only if the reaction time is considerably increased.

Experimental Section

All **NMR experiments** were performed at room temperature on the spectrometers Bruker WH 270 (with Aspect 2000, Winchester 24 megabyte disk), Bruker AM 300 (with Aspect 3000, NEC 160 megabyte disk and digital phase shifter), and Bruker AM 400 (with Aspect 3000, Winchester 24 megabyte disk and digital phase shifter). The following concentrations were used: **2**, 0.68 M in CDCl–C_6D_6 (5:1, v/v); **3**, 0.43 M in $CDCl_3$–C_6D_6 (2:1, v/v) for H,C-COSY and 0.65 M in $CDCl_3$ for C-relayed H,C-COSY experiments; **4**: 0.38 M in $CDCl_3$. Chemical shifts are given in δ from Me_4Si.

H,H-COSY: pulse sequence, 90°–t_1–90°–t_2. **2**: 64 experiments of 4 scans each; relaxation delay, 3.5 s; acquisition time, 0.64 s; spectral width, 400 Hz; number of points, 512W; sinebell multiplication in both dimensions, zero-filling to 128 W in t_1 (AM 400).

H,C-COSY: pulse sequence, 90(^{1}H)–$t_{1/2}$–180°(^{13}C)–$t_{1/2}$–Δ_1–90°(^{1}H,^{13}C)–Δ_2–t_2. **2**: 128 experiments of 8 scans each; relaxation delay, 3.5 s, Δ_1 = 3.2 ms, Δ_2 = 3.2 ms; acquisition time, 0.369 s; spectral width 5555.56 Hz; number of points, 4K; sinebell multiplication in both dimensions, zero-filling to 256W in t_1 (AM 400). **3**: 200 experiments of 64 scans each; relaxation delay, 3.5 s, Δ_1 = 3.2 ms, Δ_2 = 3.2 ms; acquisition time, 0.283 s; spectral width, 3623.19 Hz; number of points, 2K; sinebell multiplication in both dimensions, zero-filling to 512W in t_1 and to 4K in t_2 (WH 270). **4**: 128 experiments of 8 scans each; relaxation delay, 3.5 s, Δ_1 3.2 ms, Δ_2 3.2 ms; acquisition time, 0.401 s; spectral width, 5102.04 Hz; number of points, 4K; sinebell multiplication in both dimensions, zero-filling to 256W in t_1 (AM 400).

C-Relayed H,C-COSY: pulse sequence see Figure 3. **2**: 128 experiments of 128 scans each; relaxation delay, 3.5 s, Δ_1 3.2 ms, Δ_2 3.2 ms, Δ_3 3.2 ms, Δ_4 10 ms; acquisition time, 0.369 s; spectral width, 5555.56 Hz; number of points, 4K; exponential multiplication with a line broadening of 5.4 Hz in t_1 and of 2.7 Hz in t_2, zero-filling to 256W in t_1 and to 8K in t_2 (AM 400). **3**: 90 experiments of 128 scans each; relaxation delay, 3.5 s, Δ_1 3.2 ms, Δ_2 3.2 ms, Δ_3 3.2 ms, Δ_4 10 ms; acquisition time, 0.508 s; spectral width, 4032.26 Hz; number of points, 4K; exponential multiplication with a line broadening of 4 Hz in t_1 and of 2 Hz in t_2, zero-filling to 256W in t_1 and to 8K in t_2 (AM 300). **4**: 128 experiments of 128 scans each; relaxation delay, 3.5 s, Δ_1 3.2 ms, Δ_2 3.2 ms, Δ_3 3.2 ms, Δ_4 10 ms; acquisition time, 0.401 s; spectral width, 5102.04 Hz; number of points, 4K; exponential multiplication with a line broadening of 5.4 Hz in t_1 and of 2.4 Hz in t_2, zero-filling to 256W in t_1 and to 8K in t_2 (AM 400).

The **CNDO calculations** were performed on a SPERRY UNIVAC 1100/80 computer. We used a modified *QCPE 141* program, which allows the calculation of molecules up to 135 valence orbitals.

Several possible geometric configurations were considered for **1** and **3**, i.e., with the OH group either in the plane of the ring or perpendicular to it. For both molecules the most stable conformation was the planar one with the hydroxyl hydrogen atom pointing toward the 1-position. The oxygen bond angle was varied from 90° to 120° in steps of 1°. We found that an angle of 108° yielded the most stable conformation for both molecules. This geometry was also used for the calculation of **2** and **4**. All the other angles and the bond distances were standard, as described elsewhere.[24]

3,6-Di-*tert*-butyl-2-naphthol (3) and 3,6,8-Tri-*tert*-butyl-2-naphthol (4). 2-Naphthol (**1**) (30.0 g, 0.21 mol), *p*-toluenesulfonic acid (6.0 g, 0.032 mol), and toluene (100 mL) were heated to 95 °C, and isobutene was added, as described by Chasar.[10] The reaction was pursued by HPLC [Nucleosil C-18, 10 μm (4.6 × 250 mm), MeOH/H_2O (86:14, v/v), 2.5 mL/min, UV detection (254 nm)]. After 5 h and 30 min at 95 °C, **1** had disappeared; the main product was **3** at that time. The temperature was lowered to 85 °C during 11 h and 30 min and then to 80 °C during 1 h and 30 min. After 6 h at 80 °C the mixture contained ca. 75% of **4** and 25% of **3**; after 24 h at 80 °C the relative amount of **4** was >90%. The final mixture was worked up as described by Chasar[10] to precipitate 40.2 g (61%) of **4**, mp 166–167 °C (lit.[10] mp 164–167 °C) after recrystallization from hexane/heptane. The mother liquor of the initial precipitation[10] of **4** still contained **3** and **4** in a relative amount of 1:3, besides other products.

Registry No. **1**, 135-19-3; **2**, 1081-32-9; **3**, 39093-07-7; **4**, 91928-41-5; isobutene, 115-11-7.