tylammonium fluoride (1.0 mL of 1.0 M in tetrahydrofuran, 1.0 mmol) dropwise with stirring. The reaction mixture was stirred at room temperature for 1 h, diluted with water (10 mL), and extracted with ether (15 mL). The organic phase was washed with water (2 × 10 mL), dried, evaporated, and placed under vacuum (0.3 Torr) overnight.

The resulting desilylated ketone (167 mg) was heated with potassium amide (800 mg) and benzene (5 mL) at reflux under argon for 36 h. The reaction mixture was quenched with saturated ammonium chloride solution (10 mL) and diluted with pentane (10 mL). The organic phase was washed with water (2 × 10 mL) and dried. The solvent was carefully removed, and the residue was distilled in a Kugelrohr apparatus (35 °C/0.3 Torr). There was isolated 5.1 mg of clear colorless liquid shown by capillary GC and ^{1}H NMR to contain >80% 4-*tert*-butylcyclohexanone.

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^{17}O NMR Studies on Alkylindanones: Steric Effects

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Natural abundance ^{17}O NMR spectroscopic data, in acetonitrile at 75 °C, were obtained for 32 alkyl-substituted 1-indanones (**2–33**). Excellent additivity of substituent effects was observed for the ^{17}O chemical shifts of the substituted compounds. Introduction of alkyl groups proximate to the carbonyl group (7-position) produces large (21–36 ppm) downfield shifts. These downfield shifts were correlated with repulsive van der Waals energies estimated from molecular mechanics calculations. In multisubstituted indanones substituent effects are also additive, and the downfield shifts caused by alkyl groups proximate to the carbonyl are large enough to be used to distinguish between positional isomers. Examples of the combined use of ^{1}H, ^{13}C, and ^{17}O NMR chemical shifts to make structural assignments are given.

The use of ^{17}O NMR spectroscopy as a probe for a variety of structural questions is growing at a rapid pace.[1] Recent studies have shown that quantitative relationships can be developed between downfield shifts of ^{17}O NMR data and torsion angles for aromatic nitro compounds,[2] acetophenones,[3] aromatic carboxylic acids and derivatives,[4] and aryl ketones.[5] Large downfield shifts for ^{17}O NMR data of carbonyl groups on introduction of alkyl groups promixate to the carbonyl function in a variety of systems have also been reported.[3–7] Correlations between ^{17}O NMR data and in-plane bond angle distortions for hindered 3-substituted phthalic anhydrides[6] and multisubstituted phthalimides[7] have been found. Recent reports have suggested that local van der Waals interactions are responsible for deshielding shifts for several nucleii in sterically hindered systems.[8,9] More recently it has been shown that ^{17}O chemical shifts for certain rigid, planar amides, anhydrides, and quinones are correlated with their repulsive van der Waals energies.[10] Consequently, we have clearly demonstrated that downfield chemical shift changes in the ^{17}O NMR data for hindered carbonyl systems can result from two distinctly different phenomena: torsion angle rotation and, when such rotation is not possible, from repulsive van der Waals interaction.[11] Alkylindanones are rigid, planar systems, which can be studied to further assess the importance of repulsive van der Waals interactions on ^{17}O chemical shifts. Earlier, studies[12–14] in our laboratories on the chemical and physical properties of alkylindanones provided further impetus to investigate the influence of alkyl substitution on the ^{17}O chemical shifts of hindered indanones.

Results and Discussion

The 1-indanones used in this study were purchased (**1** and **18**) or synthesized as described below. Polyphosphoric acid (PPA) catalyzed cyclization of 2-methyl-3-phenyl-

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propionic acid and 3-phenylbutyric acid gave 2-methyl-1-indanone (**2**) and 3-methyl-1-indanone (**3**). 1-Indanones **4**, **6**, **7**, **12**, and **13** were available from earlier studies.[12] Friedel–Crafts acylation[15] ($AlCl_3$, 3-chloropropionyl chloride) of toluene, the xylenes, and 1,2,4-trimethylbenzene followed by sulfuric acid catalyzed cyclization of the resulting ω-chloro ketone gave indanones **5** and **8–11**. Substituted 3-arylbutyric acids, prepared by Friedel–Crafts alkylation of *m*-xylene, *p*-xylene, and 1,2,4-trimethylbenzene with aluminum chloride and β-butyrolactone or crotonic acid, were cyclized with PPA to 1-indanones **14–17**. *gem*-Dimethyl-substituted 1-indanones **19–28** were prepared by chromic acid oxidation of the corresponding indan.[13] These indans were available from earlier cyclialkylation studies using aromatic hydrocarbons (benzene,[14] toluene,[16] the xylenes,[16] *tert*-butylbenzene,[16] and 1,2,4-trimethylbenzene[17]), isoprene, and concentrated sulfuric acid. A related study provided the *tert*-butyl-3,3-dimethyl-1-indanones **29** and **30**.[18] 1-Indanones **32** and **33** were prepared by chromic acid oxidation[13] of 6-*tert*-butyl-4-ethyl-1,1-dimethylindan and 1,1,4,5,7-pentamethyl-5-*n*-propylindan. These indans were obtained by deoxygenation of 6-*tert*-butyl-1,1-dimethylindan-4-yl-1-ethanone and 1,1,4,6,7-pentamethylindan-5-yl-1-propanone.[19]

The structural identity of the above 1-indanones rests on their synthesis routes, NMR (^1H, ^{13}C, ^{17}O) spectroscopic studies, elemental analyses, and mass spectrometric data. An earlier ^1H NMR study showed that the *gem*-dimethyl proton signals of 1,1-dimethylindans undergo significant chemical deshielding (ca. δ 0.15) when these methyl groups are crowded by an adjacent aromatic methyl group.[16] Examination of the ^1H NMR spectra of all 3,3-dimethyl-1-indanones used in the current study show that deshielding of crowded *gem*-dimethyl proton signals is operative in that they appear at δ 1.55, 1.48, 1.50, and 1.50 for **21**, **24**, **26**, and **33**, respectively. Whereas the *gem*-dimethyl proton signals for **19**, **20**, **22**, **23**, **25**, and **27–31** appear in the normal δ 1.37–1.42 range. Since 3,3,5,6,7-pentamethyl-1-indanone **27** does not show a chemical shift for the *gem*-dimethyl proton signal, appearing at δ 1.37, the structural assignment from ^1H NMR data alone is unequivocal.

The unsubstituted aromatic carbons of the 1-indanones are readily detected from the intensity of their ^{13}C NMR signals and their off-resonance multiplicity. In addition, the signal for C-5 (para to carbonyl) can be discerned by a downfield shift as compared to the signal positions of other unsubstituted carbons. This information is particularly useful in distinguishing 1-indanone isomers having one or two unsubstituted aromatic carbons.

The three tetramethyl-1-indanones **21–23** provide an interesting series that illustrate the effectiveness of the combined use of ^1H, ^{13}C, and ^{17}O NMR data in assigning structures. ^1H NMR data show: *gem*-dimethyl proton signals shifted to δ 1.55 for **21** whereas those for **22** and **23** are found at δ 1.42 and 1.39, respectively; aromatic protons of **22** are isolated and appear as singlets, whereas those of **21** and **23** are attached to adjacent carbons and are coupled; C-7 protons of **21** and **22** are deshielded by the carbonyl group. ^{13}C NMR data show: unsubstituted carbons of **23** have signals at δ 120.2 (C-4) and 136.0 (C-5, para to carbonyl) whereas **21** shows signals at δ 120.8 and 129.9 with those of **22** appearing at δ 123.7 and 124.3 for the unsubstituted carbons, respectively. ^{17}O NMR data show: C-7 of **23** is substituted whereas C-7 of **21** and **22** is unsubstituted.

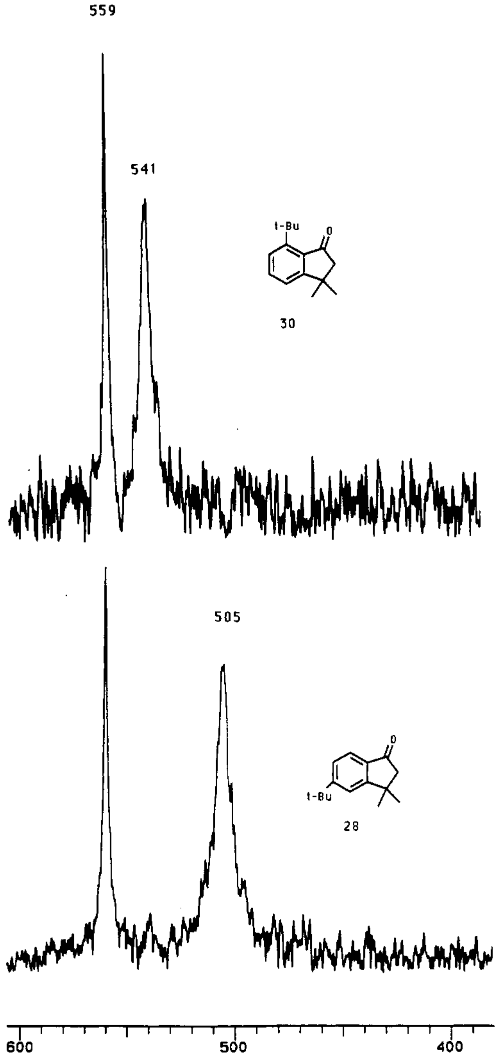

Figure 1. The ^{17}O NMR spectra of 5-*tert*-butyl-3,3-dimethylindanone (**28**) and 7-*tert*-butyl-3,3-dimethylindanone (**30**) in acetonitrile at 75 °C (1% 2-butanone, 558 ± 1 ppm, as internal standard).

The combination of ^{13}C and ^{17}O NMR data also was useful in establishing the structure of **11** as 4,5,7-trimethyl-1-indanone rather than that of the alternative isomer 4,6,7-trimethyl-1-indanone. This is based on the observed ^{17}O value as 512.6 ppm (calculated 513.4) for **11** whereas the alternative calculated value for the 4,6,7-isomer is 518.5 ppm. The ^{13}C NMR spectrum of **11** gave a signal at 131.2 ppm for the unsubstituted carbon. Had **11** been the 4,6,7-isomer, this value should have been ca. 136 ppm.

Table I contains the chemical shift data obtained from acetonitrile solutions of 30 substituted 1-indanones at 75 °C (**2–31**). Large changes in chemical shift are observed for the indanones depending upon the size and location of the substituent (Figure 1). Data for all the isomers of the monomethylindanones (**2–7**) indicate that substituent effects in this system are consistent with those noted earlier for aryl ketones and simple aliphatic ketones.[20,21] In

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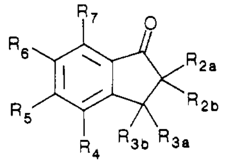
[19] The OSU authors thank Givandan Corp., Clifton, NJ, for samples of these ketones.

Table I. ^{17}O Chemical Shifts of Alkyl-Substituted Indanones[a]



compd no.	R_{2a}	R_{2b}	R_{3a}	R_{3b}	R_4	R_5	R_6	R_7	δ (C=O)
1	H	H	H	H	H	H	H	H	505.3
2	CH_3	H	H	H	H	H	H	H	499.8
3	H	H	CH_3	H	H	H	H	H	507.7
4	H	H	H	H	CH_3	H	H	H	504.8
5	H	H	H	H	H	CH_3	H	H	499.0
6	H	H	H	H	H	H	CH_3	H	504.1
7	H	H	H	H	H	H	H	CH_3	520.2
8	H	H	H	H	CH_3	H	H	CH_3	519.1
9	H	H	H	H	H	CH_3	CH_3	H	498.2
10	H	H	H	H	H	CH_3	H	CH_3	513.2
11	H	H	H	H	CH_3	CH_3	H	CH_3	512.6
12	H	H	CH_3	H	CH_3	H	H	H	507.8
13	H	H	C_2H_5	H	CH_3	H	H	H	507.0
14	H	H	CH_3	H	CH_3	H	CH_3	H	506.9
15	H	H	CH_3	H	CH_3	H	H	CH_3	524.0
16	H	H	CH_3	H	CH_3	CH_3	H	CH_3	517.9
17	H	H	CH_3	H	CH_3	H	CH_3	CH_3	521.9
18	CH_3	CH_3	H	H	H	H	H	H	494.0
19	H	H	CH_3	CH_3	H	H	H	H	510.9
20	H	H	CH_3	CH_3	H	H	H	CH_3	525.4
21	H	H	CH_3	CH_3	CH_3	CH_3	H	H	500.5
22	H	H	CH_3	CH_3	H	CH_3	CH_3	H	504.1
23	H	H	CH_3	CH_3	H	H	CH_3	CH_3	522.5
24	H	H	CH_3	CH_3	CH_3	H	H	CH_3	524.3
25	H	H	CH_3	CH_3	H	CH_3	H	CH_3	519.1
26	H	H	CH_3	CH_3	CH_3	CH_3	H	CH_3	517.0
27	H	H	CH_3	CH_3	H	CH_3	CH_3	CH_3	515.3
28	H	H	CH_3	CH_3	H	tBu	H	H	505.0
29	H	H	CH_3	CH_3	H	H	tBu	H	510.0
30	H	H	CH_3	CH_3	H	H	H	tBu	541.0
31	H	H	CH_3	CH_3	H	tBu	H	tBu	535.0

[a] Chemical shift values (±1 ppm) obtained at natural abundance in CH_3CN at 75 °C. The $^1/_2$ height widths for the signals were 290 ± 100 Hz for the methyl-substituted compounds and 400 ± 50 Hz for the *tert*-butyl-substituted ones.

comparison to the chemical shift of indanone **1**, the introduction of a methyl group α to the carbonyl, **2**, causes shielding by 5.5 ppm whereas a β-methyl group, **3**, causes modest deshielding (2.4 ppm), consistent with previously reported γ and δ effects.[20] Introduction of the methyl group into the aromatic ring produces shielding changes of 0.5, 6.3, and 1.2 ppm, respectively, consistent with electronic influences for the methyl group of **4–6**.[21] Not surprisingly, of these the largest electronic effect is noted for a methyl group on the aromatic ring when it is located in a para relationship to the carbonyl at C-5 (**6**); a 6 ppm shielding shift is observed. This shift compares very well with the 5 ppm value noted for methyl-substituted acetophenones and suggests that electronic effects are similar in the two systems.[21]

As a consequence of the ortho and para arrangements of the methyl group for the isomeric indanones **5** and **7**, the carbonyl groups of the two compounds are in electronically equivalent environments. Therefore, the 21 ppm downfield shift noted for the signal of **7** relative to **5** can be confidently attributed to steric interactions. This shift is significantly greater than the 12 ppm shift difference noted for the introduction of a methyl group in the 3-position of phthalic anhydride[6] but less than the 28 ppm shift difference observed on introduction of a methyl group in the 1-position of anthraquinone.[10]

Substituent effects appear to be remarkably additive on introduction of a second methyl group into the indanone system: compare **8–10**, **12**, **13**, **18**, and **19**. For substitution in the aliphatic portion of the system, **18** and **19**, the chemical shifts are accurately predicted when two γ and δ shift increments deduced from **1–3** are employed. For example, by using additivity of substituent effects, a value of 494.3 ppm [505.3 + 2(−5.5)] is predicted for **18**, and 494.0 ppm is the valued observed. Similarly, use of the δ values for substitution of methyl groups on the aliphatic portion of the system predicts a chemical shift of 510.1 ppm for **19** [505.3 + 2(2.4)], and a value of 510.9 ppm is observed. Additivity of substituent effects on the ^{17}O chemical shifts for multisubstitution on the aromatic portion of the ring system is observed for compounds **8–10**. Furthermore, additivity of substituent effects is noted when substitution occurs on both the aliphatic and aromatic portions of the ring system (**16**, **17**, **20–25**). For example, the value predicted for **25** is 518.7 ppm [505.3 + 2(2.4) + (−6.3) + 14.9], and the observed value is 519.1 ppm. Not unexpectedly, the prediction of chemical shift based upon additivity of substituent effects is less secure for the case **21** in which all the substituents are contiguous [predicted 503 ppm; observed 500 ppm].

In order to test further the additivity of substituent effects in multisubstituted indanones, we have obtained the ^{17}O NMR spectra for 5-*tert*-butyl-7-ethyl-3,3-dimethyl-7-ethyl-1-indanone (**32**) and 6-*n*-propyl-3,3,4,5,7-

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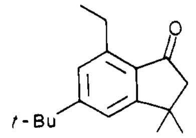
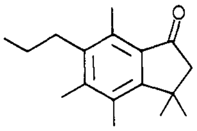
tetramethyl-1-indanone (**33**). The ^{17}O chemical shift of **32** can be predicted by using the chemical shift of 3,3-dimethylindanone (**19**) as the base (510.9 ppm), the incremental shift of a 5-tBu (−5.9 ppm), and the substituent incremental value for a 7-methyl (+14.5 ppm) for the 7-ethyl group, which leads to a predicted value of 519.5 ppm, which is in good agreement with the observed value of 518.6 ppm. In an analogous manner the chemical shift value of the multisubstituted indanone **33** can be predicted [510.9 + 14.5 − 1.2 − 6.0 − 0.5] to be 517.7 ppm which, considering the multiple substituents, is in excellent agreement with the observed value (517.3 ppm). Consequently, it appears that substituent-induced chemical shifts are additive in the indanone system over a range of alkyl substituent types and for a number of substituents.



32, 518.6 ppm



33, 517.3 ppm

The five *tert*-butyl-substituted indanones (**28**–**32**) show similar substituent effect trends for their ^{17}O chemical shift values compared to the values for their methyl-substituted analogues. The chemical shift for *tert*-butyl compounds **28** and **29** are downfield by 6 ppm from their methyl analogues **5** and **6**, which is the increment expected to arise from the *gem*-dimethyl group at position 3 (compare **1** and **19**). Internal consistency is observed for nonhindered *tert*-butyl- and methyl-substituted indanones; the chemical shift difference between **5** and **6** is 5.1 ppm and that of **28** and **29** is 5.0 ppm. In the system **30** in which the *tert*-butyl group is proximate to the carbonyl group, a large downfield chemical shift is noted. The chemical shift difference for the *tert*-butyl-substituted isomeric pair **28** and **36** is 31 ppm in comparison to 21 ppm for the methyl substituted isomeric pair **5** and **7**, which is consistent with greater repulsive van der Waals interactions expected for the larger *tert*-butyl group. The downfield shift caused by the *tert*-butyl group in the indanone system (36 ppm) is less than noted in the analogous *tert*-butylanthraquinone case, which resulted in a 49 ppm shift.[10]

Molecular mechanics calculations were carried out on the indanones **1**, **7**, and **30**, and the carbonyl group and the aromatic ring were found to be coplanar for **1** and **7**; however, a small torsion angle rotation (7°) was predicted for **30**. These calculations clearly indicate that torsion angle change is not a major contributor to the large downfield shifts observed for the hindered indanones. As we have observed in other systems,[10] the C—C=O bond angle, estimated by the MM2 method, for the hindered compounds are flared away from the substituent in the more hindered system; for example, compare 127° for **1**, 128° for **7**, and 130° for **30**. These results suggest that van der Waals interactions should play an important role in determining the chemical shifts for the hindered indanones.

Chesnut and Li have shown that repulsive van der Waals interactions could account for deshielding trends noted for ^{13}C and ^{31}P NMR data and suggested that this phenomenon should apply to other nucleii.[8,9] A correlation between deshielding shifts for ^{13}C NMR chemical data and localized steric energy was attributed to the effect of orbital size contraction on the paramagnetic screening constant. We recently reported the first relationship between ^{17}O chemical shifts and repulsive van der Waals energies of several different series of rigid, planar carbonyl systems.[10] The chemical shift data for the indanones reported here are also expected to correlate with their repulsive van der Waals energies.

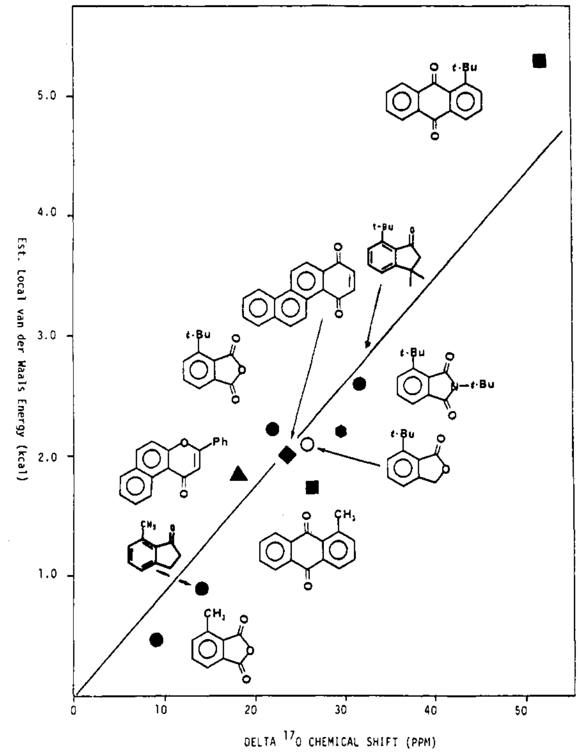


Figure 2. Relationship between estimated repulsive van der Waals interactions and ^{17}O chemical shift difference values.

In order to test for a relationship between repulsive van der Waals energy and ^{17}O chemical shift it is necessary to study systems in which steric interactions with the carbonyl group are probable; a number of compounds in Table I meet this requirement, i.e., **7**, **8**, **10**, **15**, **20**, **23**–**25**, and **30**. However, to simplify comparisons, isomers that have substituents located at electronically equivalent positions and that do not have additional steric interactions, other than the alkyl–carbonyl one, should be studied. The isomeric pairs **5**, **7** and **28**, **30** in Table I meet these criteria. As noted above, downfield shifts of 21 and 36 ppm, respectively, are observed on comparison of these isomeric pairs.

Using the approach we employed previously,[10,11] we have taken the difference in total van der Waals energy for the hindered and unhindered isomers, for example **5** and **7**, and correlated this energy with the chemical shift difference between the hindered compound and the parent of the series. Figure 2 shows a plot of the data obtained from both the methyl- and *tert*-butylindanone pairs added to data for other carbonyl systems that we reported earlier.[10] This plot further demonstrates that a reasonable relationship exists between repulsive van der Waals energies and ^{17}O chemical shifts and expands upon the wide variety of structural types for which this relationship holds. These results provide additional support for the conclusion of Chesnut and Li[8,9] that repulsive van der Waals interactions are important in determining downfield NMR chemical shifts of many nucleii in hindered systems.

Experimental Section

Except for **1** and **18** (Aldrich) the compounds studied were prepared as previously reported. All compounds were characterized by spectroscopic (^1H, ^{13}C, and ^{17}O NMR), mass spectrometric, and elemental analyses.

NMR Spectral Data, ^1H and ^{13}C ($CDCl_3$) δ for 1-Indanones. 1-Indanone (1):[21] ^1H 2.64 (t, 2), 3.15 (t, 2), 7.3–7.8 (ArH, 4); ^{13}C

25.8, 36.2, 123.7, 126.7, 127.3, 134.6, 137.1, 155.2, 207.0.

2-Methyl-1-indanone (2):[22] ^{1}H 1.30 (d, 3), 2.70 (m, 2), 3.40 (m, 1), 7.3–7.8 (ArH, 4); ^{13}C 16.3, 34.9, 42.0, 123.9, 126.5, 127.3, 134.7, 136.3, 153.5, 209.5.

3-Methyl-1-indanone (3):[22] ^{1}H 1.40 (d, 3), 2.29 (dd, 1), 2.95 (dd, 1), 3.45 (m, 1), 7.3–7.8 (ArH, 4); ^{13}C 21.3, 32.7, 45.3, 123.3, 125.3, 127.3, 134.8, 136.3, 159.9, 206.4.

4-Methyl-1-indanone (4):[22] ^{1}H 2.35 (s, 3), 2.71 (t, 2), 3.02 (t, 2), 7.2–7.6 (ArH, 3); ^{13}C 17.7, 24.6, 36.2, 121.0, 127.5, 135.0, 135.9, 136.8, 154.2, 207.4.

5-Methyl-1-indanone (5):[12a,22] ^{1}H 2.40 (s, 3), 2.65 (t, 2), 3.10 (t, 2), 7.1–7.7 (ArH, 3); ^{13}C 22.0, 25.6, 36.4, 123.5, 127.0, 128.5, 134.8, 145.7, 155.7, 206.6.

6-Methyl-1-indanone (6):[12a,22] ^{1}H 2.38 (s, 3), 2.64 (t, 2), 3.06 (t, 2), 7.3–7.6 (ArH, 3); ^{13}C 21.0, 25.4, 36.5, 123.5, 126.3, 135.8, 137.1, 137.2, 152.5, 207.0.

7-Methyl-1-indanone (7):[12a,22] ^{1}H 2.62 (s, 3), 2.66 (t, 2), 3.06 (t, 2), 7.0–7.4 (ArH, 3); ^{13}C 18.3, 25.3, 36.8, 124.0, 129.0, 133.9, 134.4, 138.8, 155.9, 207.9.

4,7-Dimethyl-1-indanone (8):[13,15] ^{1}H 2.28 (s, 3), 2.60 (s, 3), 2.64 (t, 2), 2.91 (t, 2), 6.9–7.2 (ArH, 2); ^{13}C 17.4, 18.0, 24.2, 36.6, 129.2, 132.8, 134.1, 134.4, 135.8, 154.8, 208.3.

5,6-Dimethyl-1-indanone (9):[24] ^{1}H 2.28 (s, 3), 2.34 (s, 3), 2.62 (t, 2), 3.05 (t, 2), 7.2–7.5 (ArH, 2); ^{13}C 19.7, 20.7, 25.3, 36.5, 123.9, 127.4, 135.2, 136.1, 144.7, 153.4, 206.8.

5,7-Dimethyl-1-indanone (10):[13a,23] ^{1}H 2.38 (s, 3), 2.60 (s, 3), 2.62 (t, 2), 3.00 (t, 2), 6.9–7.1 (ArH, 2); ^{13}C 18.2, 21.8, 25.2, 36.9, 124.4, 130.3, 132.3, 138.5, 144.9, 156.5, 207.4.

4,5,7-Trimethyl-1-indanone (11):[13] ^{1}H 2.20 (s, 3), 2.32 (s, 3), 2.58 (s, 3), 2.66 (t, 2), 2.95 (t, 2), 6.9 (ArH, 1); ^{13}C 13.9, 17.9, 20.1, 24.6, 37.0, 131.0, 131.2, 132.4, 135.5, 142.9, 155.0, 208.1.

3,4-Dimethyl-1-indanone (12):[12b] ^{1}H 1.33 (d, 3), 2.30 (dd, 1), 2.40 (s, 3), 2.90 (dd, 1), 3.48 (m, 1), 7.2–7.6 (ArH, 3); ^{13}C 18.1, 21.2, 32.2, 45.9, 121.1, 127.7, 135.6, 136.1, 136.1, 158.3, 206.9.

3-Ethyl-4-methyl-1-indanone (13):[12a] ^{1}H 0.87 (t, 3), 1.44 (m, 1), 1.96 (m, 1), 2.41 (s, 3), 2.48 (d, 1), 2.80 (dd, 1), 3.39 (m, 1), 7.2–7.6 (ArH, 3); ^{13}C 11.3, 18.1, 27.5, 38.9, 42.9, 121.0, 127.7, 136.0, 135.6, 136.9, 156.8, 207.1.

3,4,6-Trimethyl-1-indanone (14): mp 43–45 °C; ^{1}H 1.31 (d, 3), 2.30 (dd, 1), 2.35 (s, 3), 2.38 (s, 3), 2.91 (dd, 1), 3.45 (m, 1), 7.2–7.4 (ArH, 2); ^{13}C 18.0, 20.9, 31.9, 46.3, 121.1, 135.2, 136.4, 137.3, 137.6, 155.8, 207.1; HRMS calcd for $C_{12}H_{14}O$ (M^+) 174.1045 (found 174.1035).

3,4,7-Trimethyl-1-indanone (15):[15] ^{1}H 1.30 (d, 3), 2.28 (dd, 1), 2.45 (s, 3), 2.58 (s, 3), 2.85 (dd, 1), 3.40 (m, 1), 7.0–7.3 (ArH, 2); ^{13}C 17.7, 18.1, 21.4, 31.6, 46.4, 129.5, 132.4, 133.3, 135.4, 135.9, 158.9, 207.9.

3,4,5,7-Tetramethyl-1-indanone (16): ^{1}H 1.27 (d, 3), 2.27 (dd, 1), 2.30 (s, 3), 2.32 (s, 3), 2.56 (s, 3), 2.88 (dd, 1), 3.43 (m, 1), 6.9 (ArH, 1); ^{13}C 14.3, 18.0, 20.2, 22.1, 31.6, 46.8, 130.7, 131.4, 131.5, 135.6, 143.8, 159.4, 207.6; HRMS calcd for $C_{13}H_{16}O$ (M^+) 188.1202 (found 188.1203).

3,4,6,7-Tetramethyl-1-indanone (17): mp 62–64 °C; ^{1}H 1.27 (d, 3), 2.26 (s, 3), 2.29 (dd, 1), 2.33 (s, 3), 2.55 (s, 3), 2.89 (dd, 1), 3.37 (m, 1), 7.1 (ArH, 1); ^{13}C 13.3, 17.6, 18.9, 21.6, 30.8, 47.0, 131.7, 133.2, 134.4, 136.4, 137.6, 156.9, 208.3; HRMS calcd for $C_{13}H_{16}O$ (M^+) 188.1202 (found 188.1203).

2,2-Dimethyl-1-indanone (18): ^{1}H 1.23 (s, 6), 3.00 (s, 2), 7.3–7.8 (ArH, 4); ^{13}C 25.2, 42.8, 45.4, 124.4, 126.6, 127.4, 134.8, 135.3, 152.2, 211.2.

3,3-Dimethyl-1-indanone (19):[13b] ^{1}H 1.40 (s, 6), 2.55 (s, 2), 7.3–7.7 (ArH, 4); ^{13}C 29.9, 38.4, 52.8, 123.1, 123.5, 127.3, 134.9, 135.2, 163.2, 205.4.

3,3,7-Trimethyl-1-indanone (20):[16,25] ^{1}H 1.40 (s, 6), 2.55 (s, 2), 2.63 (s, 3), 7.0–7.5 (ArH, 3); ^{13}C 18.4, 30.1, 37.6, 53.4, 120.8, 129.1, 132.7, 134.1, 138.4, 164.6, 206.7.

3,3,4,5-Tetramethyl-1-indanone (21): ^{1}H 1.55 (s, 6), 2.36 (s, 3), 2.41 (s, 3), 2.62 (s, 2), 7.2–7.5 (ArH, 2); ^{13}C 15.7, 21.0, 28.5, 39.8, 55.5, 120.8, 129.9, 133.9, 134.6, 145.7, 160.0, 205.8. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.24; H, 8.52.

3,3,5,6-Tetramethyl-1-indanone (22): mp 84–86 °C; ^{1}H 1.42 (s, 6) 2.30 (s, 3), 2.36 (s, 3), 2.56 (s, 2), 7.2–7.5 (ArH, 2); ^{13}C 19.7, 20.9, 30.0, 38.1, 53.2, 123.9, 124.3, 133.5, 136.3, 145.1, 162.1, 205.7. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.89; H, 8.58.

3,3,6,7-Tetramethyl-1-indanone (23): mp 69–70 °C; ^{1}H 1.39 (s, 6), 2.32 (s, 3), 2.57 (s, 2), 2.59 (s, 3), 7.2–7.4 (ArH, 2); ^{13}C 13.7, 19.0, 30.2, 36.8, 53.9, 120.2, 132.6, 136.0, 136.2, 136.9, 162.6, 207.3. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.41; H, 8.67.

3,3,4,7-Tetramethyl-1-indanone (24): mp 40–42.5 °C; ^{1}H 1.48 (s, 6), 2.46 (s, 3), 1.56 (s, 2), 1.56 (s, 3), 7.0–7.2 (ArH, 2); ^{13}C 18.4, 19.4, 28.1, 38.9, 55.4, 129.7, 132.3, 133.5, 136.3, 137.0, 160.5, 207.1. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.76; H, 8.35.

3,3,5,7-Tetramethyl-1-indanone (25):[25] ^{1}H 1.37 (s, 6), 2.39 (s, 3), 2.54 (s, 2), 2.59 (s, 3), 6.9–7.1 (ArH, 2); ^{13}C 18.3, 22.0, 30.1, 37.5, 53.7, 121.3, 130.4, 130.6, 138.2, 145.2, 165.2, 206.2.

3,3,4,5,7-Pentamethyl-1-indanone (26):[17] ^{1}H 1.50 (s, 6), 2.30 (s, 3), 2.35 (s, 3), 2.55 (s, 3), 2.56 (s, 2), 6.90 (ArH, 1); ^{13}C 15.4, 18.2, 20.7, 28.6, 38.8, 56.1, 130.9, 131.9, 132.0, 135.6, 144.7, 160.6, 206.5.

3,3,5,6,7-Pentamethyl-1-indanone (27):[16] ^{1}H 1.37 (s, 6), 2.20 (s, 3), 2.37 (s, 3), 2.53 (s, 2), 2.62 (s, 3), 7.1 (ArH, 1); ^{13}C 13.9, 14.6, 22.0, 30.2, 36.7, 54.0, 121.9, 130.8, 134.9, 136.6, 144.0, 162.3, 206.9.

5-*tert*-Butyl-3,3-dimethyl-1-indanone (28):[16] ^{1}H 1.35 (s, 9), 1.40 (s, 6), 2.59 (s, 2), 7.4–7.7 (ArH, 3); ^{13}C 30.0, 31.3, 35.6, 38.6, 53.3, 119.7, 122.9, 125.2, 133.0, 159.2, 164.1, 205.5.

6-*tert*-Butyl-3,3-dimethyl-1-indanone (29):[13b] ^{1}H 1.34 (s, 9), 1.42 (s, 6), 2.61 (s, 2), 7.3–7.7 (ArH, 3); ^{13}C 30.0, 31.4, 34.8, 38.1, 53.4, 119.6, 123.1, 132.8, 135.2, 150.8, 161.4, 206.4.

7-*tert*-Butyl-3,3-dimethyl-1-indanone (30):[18] ^{1}H 1.38 (s, 6), 1.47 (s, 9), 2.58 (s, 2), 7.0–7.5 (ArH, 3); ^{13}C 29.8, 30.3, 35.8, 37.1, 53.9, 121.4, 124.6, 132.9, 134.3, 151.6, 166.9, 205.4.

5,7-Di-*tert*-butyl-3,3-dimethyl-1-indanone (31): ^{1}H 1.38 (s, 9), 140 (s, 6), 1.47 (s, 9), 2.56 (s, 6), 7.32 (d, 1), 7.41 (d, 1); ^{13}C 29.8, 30.4, 31.2, 35.7, 36.0, 37.2, 54.3, 117.7, 122.4, 130.5, 150.9, 158.0, 167.3, 205.0; HRMS calcd for $C_{19}H_{28}O$ (M^+) 272.2140 (found 272.2135).

5-*tert*-Butyl-3,3-dimethyl-7-ethyl-1-indanone (32):[18] ^{1}H 1.24 (t, 3), 1.36 (s, 9), 1.40 (s, 6), 2.55 (s, 2), 3.06 (q, 2), 7.2–7.3 (ArH, 2); ^{13}C 15.1, 25.2, 30.2, 31.3, 35.5, 37.7, 53.9, 117.3, 125.1, 129.9, 144.2, 158.5, 165.1, 205.9; HRMS, calcd for $C_{17}H_{24}O$ (M^+) 244.1828 (found: 244.1831).

3,3,4,5,7-Pentamethyl-6-*n*-propyl-1-indanone (33): mp 70–71 °C; ^{1}H 1.04 (t, 3), 1.47 (m, 2), 1.50 (s, 6), 2.28 (s, 3), 2.38 (s, 3), 2.56 (s, 2), 2.62 (s, 3), 2.65 (t, 2); ^{13}C 13.7, 14.6, 16.6, 16.7, 22.7, 28.7, 31.6, 38.0, 56.5, 131.2, 131.3, 134.1, 139.9, 143.3, 158.1, 207.3; HRMS calcd for $C_{17}H_{24}O$ (M^+) 244.1828 (found: 244.1839).

The ^{17}O NMR spectra were recorded on a JEOL GX-270 or on a Varian VXR-400 spectrometer equipped with a 10-mm broad-band probe. All spectra were acquired at natural abundance at 75 °C in acetonitrile (Aldrich, anhydrous gold label under nitrogen) containing 1% of 2-butanone as an internal standard. The concentration of the ketones employed in these experiments was 0.5 M. The signals were referenced to external deionized water at 75 °C. The 2-butanone resonance (558 ± 1 ppm) was used as an internal check on the chemical shift measurements for these compounds. The instrumental settings for the GX-270 at 36.5 MHz were as follows: spectral width 25 kHz, 2K data points, 90° pulse angle (28-ms pulse width), 200-ms acquisition delay, 40-ms acquisition time, and 40 000–100 000 scans were required. The instrumental settings for the VXR-400 at 54.22 MHz were as follows: spectral width 35 kHz, 2K data points, 90° pulse angle (40-ms pulse width), 200-ms acquisition delay, 29-ms acquisition time, and 30 000–60 000 scans. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a 25-Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to ±0.1 ppm on the VXR-400 and ±0.2 ppm on the GX-270 by zero filling to 8K data points. The reproducibility of the chemical shift data is estimated to be better than ±1.0 ppm.

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Absolute Electronegativity and Hardness: Applications to Organic Chemistry

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The recent concepts of absolute electronegativity, χ, and absolute hardness, η, are briefly reviewed. Experimental values for a large number of molecules and radicals are presented. The values are shown to be in good agreement with the known chemical behavior, both as to nucleophilic–electrophilic properties and as to rates of reaction. Applications are also given for the use of empirical rank orders of the local hardness, $\tilde{\eta}$. The uses of χ and η are consistent with frontier orbital theory. To make meaningful comparisons in a series of molecules, it is necessary that these orbitals remain the same. Also it is necessary that the observed I and A values of the molecules relate to the appropriate frontier orbitals.

The concept of hard and soft Lewis acids and bases was applied to organic chemistry in 1967.[1] A number of interesting, but qualitative, correlations were made.[2] A serious problem was that the terms hard and soft were not well defined, either theoretically or experimentally. Recently this deficiency has been corrected.[3] With use of density functional theory as a basis, the hardness of a chemical system has been rigorously defined. At the same time a related property, the electronic chemical potential, has been introduced.[4]

Any chemical system (atom, molecule, ion, radical) is characterized by its electronic chemical potential, μ, and by its absolute hardness, η. The exact definition of these quantities are

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v \quad \eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v \tag{1}$$

where N is the number of electrons and v is the potential due to the nuclei, plus any external potential.

Operational and approximate definitions are

$$-\mu = (I + A)/2 = \chi \qquad \eta = (I - A)/2 \tag{2}$$

where I is the ionization potential and A is the electron affinity.

Since $(I + A)/2$ is the Mulliken electronegativity for atoms, the value for any system, χ, is called the absolute electronegativity. For an equilibrium system it must be constant everywhere. The hardness, η, need not be constant and can have local values, but $(I - A)/2$ is the average or global value. The softness, σ, is simply the inverse of the hardness, $\sigma = 1/\eta$.

If two systems, B and C, are brought together, electrons will flow from that of lower χ to that of higher χ, until the chemical potentials become equal. As a first approximation, the (fractional) number of electrons transferred, ΔN, will be given by

$$\Delta N = \frac{\chi_C - \chi_B}{2(\eta_C + \eta_B)} \tag{3}$$

Obviously this is a convenient way of looking at generalized acid–base reactions

$$C + {:}B \rightarrow C{:}B \tag{4}$$

where C is the Lewis acid. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance.

There is an energy lowering due to electrons being transferred to a lower chemical potential. But this is only a small part of the total energy change, which must also include covalent bonding and ionic interactions. Even though (3) is incomplete, it is still useful because it measures the initial interaction between B anc C by using only properties of the isolated systems. Furthermore we can assume that the covalent bonding will show some proportionality to ΔN, since coordinate covalent bonding is involved. For neutral reactants the ionic binding will also depend on ΔN.

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