respectively, plus residual absorptions from $Cp^*Re(CO)_3$. Further irradiation intensified the absorptions from **2** relative to **1**. Following chromatography on neutral alumina and crystallization at −78 °C, compounds **1**, *exo*-**2**, and *endo*-**2** (ratio exo:endo = 5:1 at 5 °C) were separated and fully characterized. Irradiation of **1** alone (hexane, quartz tube) under a propene purge gave **2** as the main product, but under a N_2 purge only a low yield of **2** resulted, suggesting that photodissociation of propene from **1** is a competing reaction.

Crystals of *exo*-**2** and *endo*-**2** are composed of equal amounts of the *R*- and *S*- enantiomers (Figure 1). In both cases the hydride position was located. The η^3-allyl group is symmetrically bonded to Re in *exo*-**2** with distances Re–C(6) = 2.260 (9) Å and Re–C(8) = 2.257 (10) Å to the terminal carbons and Re–C(7) = 2.179 (9) Å to the central carbon atom; however, in *endo*-**2** the allyl group is somewhat asymmetrically bonded, with distances Re–C(6) = 2.191 (9) Å and Re–C(8) = 2.242 (9) Å to the termini and Re–C(7) = 2.215 (9) Å. This is reflected in the carbon–carbon bond lengths of the allyl group which are equal within error in *exo*-**2** (C(6)–C(7) = 1.374 (16) Å; C(7)–C(8) = 1.363 (17) Å) but differ in *endo*-**2** (C(6)–C(7) = 1.446 (13) Å; C(7)–C(8) = 1.386 (13) Å). The carbon atom C(6) that is pseudotrans to hydride ligand is the one having shorter Re–C and longer C–C bond lengths in *endo*-**2**.

Two previous X-ray structures of (η^3-allyl) hydrido compounds have been published,[2,5] but only for $IrHCl(\eta^3\text{-}CH_2CHCHPh)(PPh_3)_2$ has the hydride been located and full structural details published.[2] The allyl ligand is asymmetrically bonded in this complex, but this may be partly a consequence of the phenyl group. The existence of two isomers of the allyl(hydrido) complex $[Ir(H)(C_3H_5)(PMe_3)_3]^+$, postulated to involve different rotational orientations of the allyl group, was not confirmed.[7]

Exo and endo isomeric forms for the allyl ligand in cyclopentadienyl complexes with piano-stool structures like **2** have been amply studied, notably by Faller and co-workers.[13] While X-ray structures have been determined for either exo or endo forms of several such compounds,[14] in the present case structures have been obtained on both exo and endo forms of the same compound, providing the opportunity for a detailed comparison of the ligand in its two orientations.[14h] Although the ligand is slightly asymmetrically bound in the endo isomer, there is no doubt that it is nevertheless a true η^3-allyl group rather than a σ–π allyl as found, for example, for the very asymmetrically bound group in *endo*-$CpMo(NO)(I)(\eta^3\text{-}C_3H_5)$ and its tungsten analogue.[14f,g]

The ^1H NMR spectra of the two isomers have been completely assigned by decoupling and NOE procedures, and these also show interesting differences. For the symmetrically bound η^3-allyl ligand in *exo*-**2** the resonances of all five inequivalent hydrogens are in the range 1.76–2.57 ppm. For the endo isomer the resonances occur either side of this range; anti hydrogens H_2 and H_3 have smaller δ values (0.25 and 0.65 ppm, respectively), while the syn hydrogens H_1 and H_4 have larger δ values (2.67 and 3.26 ppm, respectively), and H_5 (4.01 ppm) is greatest. This contrasts with results for exo and endo isomers of $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ where the most prominent difference was a shift of the anti protons of the endo isomer to larger δ compared with the exo isomer.[13a] It also differs from results for the very asymmetrically bound allyl group in $CpMo(NO)(I)(\eta^3\text{-}C_3H_5)$ where in both exo and endo isomers both protons of one terminus (the allylic protons) resonate at low δ, well separated from the vinylic protons at higher δ values.[14f,g]

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Supplementary Material Available: Analytical and spectroscopic data for **1** and **2** and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and selected bond distances and angles for *exo*-**2** and *endo*-**2** (12 pages); tables of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(13) See, for example: (a) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840. (b) Faller, J. W.; Chen, C. C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361. (c) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388.

(14) For examples of *exo*- or *endo*-η^3-allyl structures, see: (a) Vanarsdale, W. E.; Kochi, J. K. *J. Organomet. Chem.* **1986**, *317*, 215 (exo). (b) Faller, J. W.; Chao, K. H. *Organometallics* **1984**, *3*, 927. (c) Carré, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 970 (mixture of isomers). (d) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400 (exo). (e) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251 (*endo*-allyl and *exo*-cyclooctenyl). (f) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227 (*exo*-$CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ and *endo*-$CpMo(NO)(I)(\eta^3\text{-}C_3H_5)$). (g) Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268 (*endo*-$CpW(NO)I(\eta^3\text{-}C_3H_5)$). (h) Hsu, L.-Y.; Nordman, C. E.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1989**, *8*, 241.

Graph Theoretical Approach to Carbon-13 Chemical Shift Sum in Alkanes

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In structural chemistry molecules can conveniently be viewed as graphs. A wide variety of different graph theoretical indices have been devised[1-4] and used in structure-property and structure-activity studies.[5-10] In the present study we have found that an integer graph theoretical index *L* which is a simple linear combination of molecular path counts of length one, p_1, length two, p_2, and length three, p_3, for carbon atoms of alkanes is well correlated with a summation of carbon-13 atomic chemical shifts.

In an earlier study, Wiener[11] first introduced a path number *W* and a polarity number p_3 to find a correlation for the boiling points of alkanes. *W* was defined as the total number of bonds between all pairs of carbon atoms in an alkane molecule. p_3 was defined as the number of ways in which an alkane C–C–C–C fragment can be superimposed on the alkane molecule and is equal to the path counts of length three. Wiener applied his analysis also to molecules having heteroatoms. The Gordon–Scantlebury[12] index p_2 was proposed to characterize molecular branching in hydrocarbons. p_2 is equal to the path count of length two. Randič and Wilkins[13] reported that the regular variations in numerous thermodynamic properties of alkane isomers have been demonstrated by considering only p_2 and p_3.

Grant and Paul[14] and Lindeman and Adams[15] found the additivity expression for carbon-13 chemical shifts for atoms in alkanes. In contrast to the additivity of the chemical shift study,

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(1) Hosoya, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2332–2339.

(2) Rouvray, D. H. In *Chemical Application of Topology and Graph Theory*; King, R. B., Ed.; Elsevier: Amsterdam, 1983; pp 159–177.

(3) Bertz, S. H.; Herndon, W. C. In *Artificial Intelligence Applications in Chemistry*; Pierce, T. H., Hohne, B. A., Eds.; ACS Symposium Series 306; American Chemical Society: Washington, DC, 1986; pp 169–175.

(4) Randič, M. *J. Chem. Inf. Comput. Sci.* **1988**, *28*, 142–147.

(5) Trinajstic, N. *Chemical Graph Theory. II*; CRC Press: Boca Raton, FL, 1983; pp 105–140.

(6) Takahashi, Y.; Miyashita, Y.; Tanaka, Y.; Hayasaka, H.; Abe, H.; Sasaki, S. *J. Pharm. Sci.* **1984**, *73*, 737–741.

(7) Basak, S. C. *Med. Sci. Res.* **1987**, *15*, 605–609.

(8) Okuyama, T.; Miyashita, Y.; Kanaya, S.; Katsumi, H.; Sasaki, S.; Randič, M. *J. Comput. Chem.* **1988**, *9*, 636–646.

(9) Needham, D. E.; Wei, I.; Seybold, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 4186–4194.

(10) Gao, Y.; Hosoya, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3093–3102.

(11) Wiener, H. *J. Am. Chem. Soc.* **1947**, *69*, 17–20.

(12) Gordon, M.; Scantlebury, G. R. *Trans. Faraday Soc.* **1964**, *60*, 604–621.

(13) Randič, M.; Wilkins, C. L. *J. Phys. Chem.* **1979**, *83*, 1525–1540.

(14) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984–2990.

(15) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245–1252.

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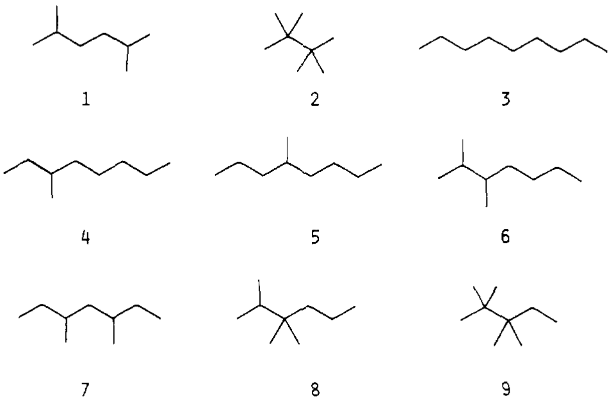

Figure 1. Molecular graphs for alkanes having the same L index 15.

Table I. Molecular Path Counts p_1, p_2, and p_3 and Carbon-13 Chemical Shift Sums for Alkanes with L = 15

no.	p_1	p_2	p_3	chemical shift sum (ppm)
1	7	8	5	220.2
2	7	12	9	223.6
3	8	7	6	225.4
4	8	8	7	226.9
5	8	8	7	228.6
6	8	9	8	225.1
7	8	9	8	228.8
8	8	11	10	227.2
9	8	13	12	229.1

which accounts for a single molecule, Randič[16] reported that sums of carbon-13 chemical shifts for all atoms in 18 octanes correlate with molecular path counts. He found that p_2 makes a positive contribution, while p_3 makes a negative one to the molecular isomeric variations. Recently Randič and Trinajstic[17] have found that the difference $(p_2 - p_3)$ leads to a correlation of mean carbon-13 chemical shifts in octanes and nonanes. However, they did not report the regularities of chemical shift sums for molecules of diverse composition and constitution. Randič[18] also found the regularities of carbon-13 chemical shifts for individual atoms in alkanes.

We have extended the work of Randič[16] on the chemical shift sums and found a simple relation between an integer graph theoretical index L and the chemical shift sum. L is defined as

$$L = 2p_1 + p_2 - p_3 - 2 \tag{1}$$

The experimental chemical shift values for 64 alkanes[13,14] from C_2 through C_{10} relative to tetramethylsilane were used in this study. The relatively large spread of the values for carbon-13 chemical shift sums, from 11.4 for ethane to 312.1 for 2,2,4,4-tetramethylpentane was observed. The molecular path counts p_1, p_2, and p_3 and carbon-13 chemical shift sums for nine alkanes with L = 15 are shown in Table I. The molecular graphs for these alkanes are shown in Figure 1. It is worthy to remark that the skeletal forms shown in Figure 1 are so distinctive, and there is not a priori reason to expect that these molecules will share any common characteristics; however the present work points out that they have common chemical shifts sum.

In Figure 2 we plotted the chemical shift sum $\sum\delta$ against the L index for 64 alkanes. All the points of the plot in this figure can be fitted reasonably well on one straight line. $\sum\delta$ has been shown to be proportional to L:

$$\sum\delta \propto L \tag{2}$$

Using a least-squares regression analysis, we computed the slope of this straight line. The slope was found to be 14.9 ppm, and the correlation coefficient was 0.992. The predicted chemical shift sum for the alkanes with L = 15 shown in Table I is 223.5 ppm.

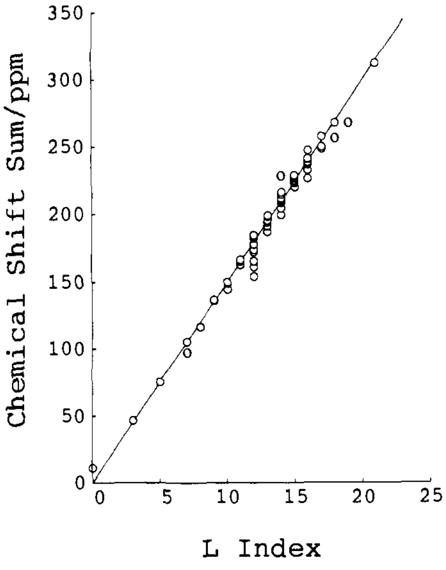

Figure 2. Plot of the carbon-13 chemical shift sum against the L index for alkanes from C_2 to C_{10}.

From eq 1, it is easy to understand the effect of path counts on the chemical shift sum: p_1 and p_2 make a positive contribution, while p_3 makes a negative one to the diverse homological variations in alkanes. The new graph theoretical index L is useful for classifying alkanes into global C-13 nuclear magnetic categories. The simple sum of chemical shift in the alkane has been shown to be one of the characteristic molecular properties which reflect simple but relevant features.

In summary, a novel relationship between molecular path counts and chemical shift sums has been discovered. Details of this work concerning the relation between the additivity of individual chemical shifts for atoms and chemical shift sums in alkanes and statistical analysis are being published elsewhere.

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(16) Randič, M. *J. Magn. Reson.* **1980**, *39*, 431-436.
(17) Randič, M.; Trinajstic, N. *Theor. Chim. Acta* **1988**, *73*, 233-246.
(18) Randič, M. *Int. J. Quantum Chem.* **1983**, *23*, 1707-1722.

Photomodulation of Polypeptide Conformation by Sunlight in Spiropyran-Containing Poly(L-glutamic acid)

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Photochromic vinyl polymers, such as polyacrylates containing spiropyran groups, were found to undergo photoinduced variations of their viscosity.[1-4] Since the viscosity of a polymer system is

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(1) Irie, M.; Menju, A.; Hayashi, K.; Smets, G. *J. Polymer Sci., Polymer Lett. Ed.* **1979**, *17*, 29-31.
(2) Irie, M.; Menju, A.; Hayashi, K. *Macromolecules* **1979**, *12*, 1176-1180.
(3) Irie, M.; Hayashi, K.; Menju, A. *Polymer Photochem.* **1981**, *1*, 233-242.