different solutions, whereas with an empty blackboard the direction of the agents' searches is highly focused by the first few arriving hints. Also, we observed that a nonempty initial blackboard leads to a smaller range of speeds because, with many hints already available, the importance of hint selection strategy becomes less important.

In conclusion, we have shown how cooperating toward the solution of a constraint satisfaction problem can increase the speed with which it is solved as compared to either the noncooperating case or a partitioned problem space, even with very simple agents and hints. The resulting distribution of performance agrees with the theoretical predictions and provides a quantitative assessment of the value of cooperating in problem solving. These agents were very sensitive to the first few hints. There remains the question of how much individual expertise is required to give more reproducible results. This would allow prediction of μ and σ, and hence scaling with the number of agents.

The way agents interpret their hints has a strong effect on the rate at which they solve the problem. This is especially so for the fastest and slowest agents. For a sufficiently large number of agents, the group with the highest diversity in interpretation was able to solve the problem first. Interestingly, high diversity not only leads to very fast performers but to very slow ones as well. These slow performers are necessary because they provide some hints used by the fastest agents.

This work suggests an alternative to the current mode of constructing task-specific computer programs that deal with constraint satisfaction problems. Rather than spending all the effort in developing a monolithic program or perfect heuristic, it may be better to have a set of relatively simple cooperating processes work concurrently on the problem while communicating their partial results. This would imply the use of "hint engineers" for coupling previously disjoint programs into interacting systems that can use each other's (imperfect) knowledge.

Because our results confirm a theory that provides a quantitative relation between performance, number of agents, and the ability of agents to use diverse hints, this new methodology may be particularly useful in areas of artificial intelligence such as design, qualitative reasoning, truth maintenance systems, and machine learning. Researchers in these areas are just starting to consider the benefits brought about by massive parallelism and concurrency.

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10. This work was supported in part by Air Force Office of Scientific Research contract F49620-90-C-0086.

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Radical Reactions of C_{60}

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Photochemically generated benzyl radicals react with C_{60} producing radical and nonradical adducts R_nC_{60} ($R = C_6H_5CH_2$) with $n = 1$ to at least 15. The radical adducts with $n = 3$ and 5 are stable above 50°C and have been identified by electron spin resonance (ESR) spectroscopy as the allylic $R_3C_{60}^{\cdot}$ (3) and cyclopentadienyl $R_5C_{60}^{\cdot}$ (5) radicals. The unpaired electrons are highly localized on the C_{60} surface. The extraordinary stability of these radicals can be attributed to the steric protection of the surface radical sites by the surrounding benzyl substituents. Photochemically generated methyl radicals also add readily to C_{60}. Mass spectrometric analyses show the formation of $(CH_3)_nC_{60}$ with $n = 1$ to at least 34.

THE RECENT DISCOVERY THAT C_{60} can be produced in macroscopic quantities (*1*) has sparked much interest in the chemistry of this unusual molecule. An important aspect of the chemistry of C_{60} is its reactivity towards free radicals. The molecule has, in effect, 30 carbon-carbon double bonds to which free radicals can add. Our previous results (*2*) indicated that multiple additions of a variety of radicals can indeed take place very readily, warranting characterization of this molecule as a radical sponge. No structural information was available, however. Here we identify by electron spin resonance (ESR) two extraordinarily stable, prototypical radical types formed in the addition of benzyl radicals to C_{60}. Crucial to the analysis of the complex mixture was information obtained by: (i) ^{13}C labeling of the entering benzyl radicals in the α position; and (ii) the different ESR power saturation behavior of the two radical structures. The latter allowed selection of either spectrum simply by varying the microwave power level.

C_{60} dissolves in a limited number of organic solvents, notably toluene. Since this solvent is susceptible to attack by photolytically generated *tert*-butoxy radicals with the formation of benzyl radicals (*3*), we used this route to study the addition of benzyl radicals to C_{60}.

$$(CH_3)_3CO\text{–}OC(CH_3)_3 \xrightarrow[\text{Toluene}]{h\nu} 2\,(CH_3)_3CO^{\cdot}$$

$$C_6H_5CH_3 + (CH_3)_3CO^{\cdot} \rightarrow C_6H_5CH_2^{\cdot} + (CH_3)_3COH$$

In a typical experiment, 50 μl of di-*tert*-butyl peroxide were added to 350 μl of a saturated (~3 mM) solution of C_{60} in sodium-dried, oxygen-free toluene in a quartz ESR tube. The solution was then irradiated at various temperatures in the cavity of an ESR spectrometer. Focused ultraviolet light (UV) of a high-pressure mercury discharge lamp was used that was filtered to remove the visible and much of the infrared radiation by an aqueous $NiSO_4$-$CoSO_4$ filter (*4*).

The UV irradiation of such solutions at room temperature produced a single ESR absorption that grew steadily to a maximum and that did not decay when the light was extinguished. This absorption had a most unusual microwave power saturation behavior. Unlike the ESR spectra of most carbon-centered radicals, the spectrum did not power saturate even with the full output of the microwave source (~200 mW). Also, the *g* factors measured at high (200 mW) and at low (200 μW) incident powers were significantly different (2.00221 and 2.00250, respectively) so that the absorption shifted noticeably (~0.5 G) along the magnetic

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field axis simply by changing the microwave power. Evidently, the overall absorption belongs to at least two species, one that power saturates readily and one that does not. The ^{13}C (natural abundance 1.1%) satellite lines were sought at higher gains. The broader absorption at high power displayed no ^{13}C satellites, whereas the narrower absorption at low power did. With perdeuterotoluene at 50°C and low power, a reduction in linewidth allowed the observation of three pairs of ^{13}C satellites with hyperfine splittings of 19.8, 13.1, and 9.7 G.

The same experiment was performed with toluene enriched to 99% with ^{13}C on the benzylic carbon. The radical species were generated at 50°C, where less stable radical adducts decay and the ESR lines narrow. At low power, coupling occurred to three ^{13}C nuclei, two of which are equivalent: $a(2C) = 9.70$ G (triplet), $a(1C) = 1.75$ G (doublets) with $g = 2.00221$ and $\Delta H = 0.5$ G (Fig. 1A). At high power, a sextet was obtained ($g = 2.00221$, $\Delta H = 1.7$ G) with intensities indicating five equivalent ^{13}C nuclei: $a(5C) = 3.56$ G (Fig. 1B).

We assigned the low-power spectrum to an allylic radical arising from the addition of three benzyl radicals to adjacent double bonds radiating from a five-membered ring [structure **3** ($R = C_6H_5{}^{13}CH_2$) in Scheme 1]. No evidence was obtained for the first-formed radical adduct **1**, which is probably short-lived. The spectrum of radical **3** probably cannot be distinguished from those of similar radicals having an additional even number of benzyl radicals elsewhere on the surface of the C_{60} molecule. The two strongly interacting ^{13}C nuclei of the R_1 and R_3 benzyl groups (9.7 G) are favorably placed for substantial hyperconjugative interaction (*5*) with the terminal allylic carbons. In the parent allyl radical, these have positive spin density of about +0.58 (*5*). The curvature of the structure may change this interaction compared to the planar model. The single, weakly interacting ^{13}C nucleus of R_2 (1.75 G) is similarly positioned with respect to the central allylic carbon, where a smaller, negative spin density is expected [about −0.16 in allyl (*5*)]. The remaining two ^{13}C hyperfine interactions of 19.8 and 13.1 G (Fig. 1B) were assigned to the terminal and central allylic carbon nuclei of the C_{60} skeleton, respectively. The corresponding interactions in the parent allyl radical are 21.93 and 17.21 G with $g = 2.00252$ (*6*).

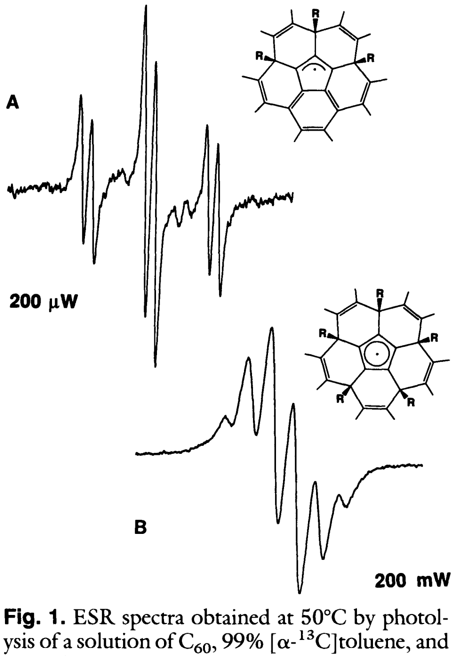


Fig. 1. ESR spectra obtained at 50°C by photolysis of a solution of C_{60}, 99% [α-^{13}C]toluene, and di-*tert*-butylperoxide at (**A**) 200 μW and (**B**) 200 mW of incident microwave power.

We assigned the sextet spectrum observed at high microwave power to the cyclopentadienyl radical **5**, resulting from the addition of five benzyl radicals to C_{60} (Scheme 1). The unpaired electron is shared equally by the carbon atoms of a five-membered ring. Again, we cannot exclude similar structures having an additional even number of benzyl groups elsewhere on the surface of C_{60}. The cyclopentadienyl radical and $R_5C_{60}{}^{\bullet}$ have electronically degenerate ground states due to the fivefold axes of symmetry. Because of strong spin-orbit coupling and an attendant efficient spin relaxation, such orbitally degenerate carbon-centered radicals typically have broader lines than nondegenerate radicals and do not power saturate readily, as observed here. The interaction of the five ^{13}C nuclei associated with the methylene groups of the entering benzyl radicals (3.56 G) is again of the hyperconjugative type. It is smaller than for the methylene carbons of R_1 and R_3 in **3** because the spin density on each carbon of the cyclopentadienyl moiety (0.20 in the parent cyclopentadienyl radical) is less than that on the terminal allylic carbons in **3**. The lack of ^{13}C satellite lines associated with the C_{60} framework is consistent with the small ^{13}C hyperfine interaction in the cyclopentadienyl radical (2.7 G) (*7*). With $\Delta H = 1.7$ G, satellite lines for ^{13}C in natural abundance with a splitting of this magnitude would be buried under the spectrum of the main isotopic species.

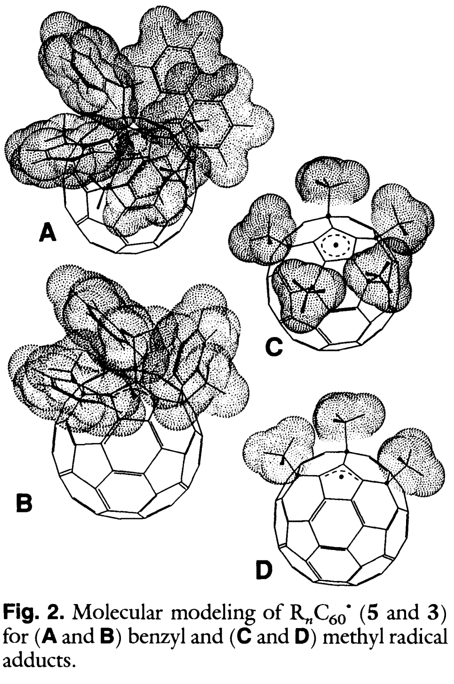
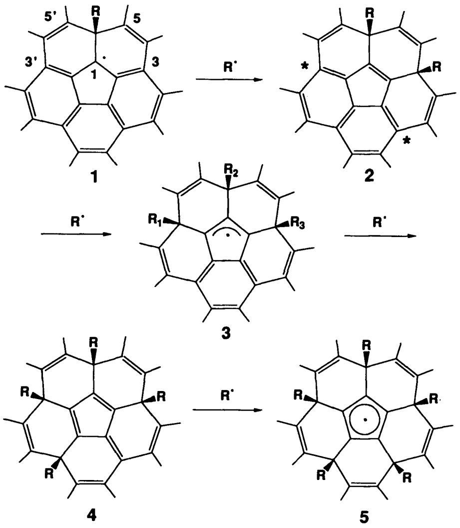


Fig. 2. Molecular modeling of $R_nC_{60}{}^{\bullet}$ (**5** and **3**) for (**A** and **B**) benzyl and (**C** and **D**) methyl radical adducts.



Scheme 1. Radical formation.

If we assume that the configurations of the benzyl groups relative to the nearest radical carbons (α-carbons) are approximately the same in **3** and **5**, then the ratios of the ^{13}C hyperfine splittings of the benzylic carbons in **3** and **5**, that is $9.7/3.5 = 2.77$ and $1.75/3.5 = 0.50$, should approximate the ratios of the absolute values of the spin densities at the α-carbons (*8*). Because the spin density on each α-carbon of **5** is ~0.20, one obtains $0.20 \times 2.77 = 0.55$ and $0.20 \times 0.50 = 0.10$ for the spin densities on the terminal and central allylic carbons of **3**. The reasonable agreement with the absolute values of the corresponding spin densities in the parent allyl radical (0.58 and 0.16) indicates that **3** is quite similar to the allyl prototype despite the complexities of the system such as curvature and adjacent double bonds. The substantial localization of the unpaired electron in **3**, even in the presence of the remaining unsaturation, is noteworthy. The olefinic units appear to be weakly conjugated.

We attribute the extraordinary stability of radicals **3** and **5** to the steric protection afforded by three or five benzyl groups sheltering the radical sites. The inaccessibility of the unpaired electron in Fig. 2, A and B (*9*), can be compared with the more open structures and likely greater reactivity of the corresponding methyl derivatives in Fig. 2, C and D.

The reaction pathway leading to **3** and **5** in Scheme 1 follows from considerations of steric hindrance, radical pairing, and the likely participation of the more reactive double bonds. The initially formed radical **1** probably has a brief existence. It is consumed by reaction with R˙ continuously generated by photolysis. The unpaired electron in **1** is mostly localized on carbon 1 (Scheme 1) (*10*) and to a lesser extent on C3(3′) and C5(5′) (*11*). Extensive delocalization of the unpaired electron on the surface of **1** is excluded. Thus, reaction with another R˙ to yield the nonradical product **2** occurs preferentially at C3(3′), rather than at C1 or C5(5′), to avoid unfavorable 1,2 (vicinal) steric interactions. Another R˙ can now add anywhere on **2**. However, the newly formed double bond is partially conjugated with only two other olefinic units and is more likely to participate in the next addition of R˙ than the undisturbed double bonds elsewhere on **2**. Accordingly, addition to C* affords the observed allylic radical **3**, which is resonance and sterically stabilized. The usual driving force to pair electrons leads the next radical to add as shown. The result is a pseudofulvene **4**, which should be highly susceptible to radical addition to form the resonance-stabilized cyclopentadienyl radical **5**. The latter is inert to further radical attack as it is protected by a canopy of benzyl substituents (Fig. 2A). Reaction elsewhere on the C_{60} surface is then preferred.

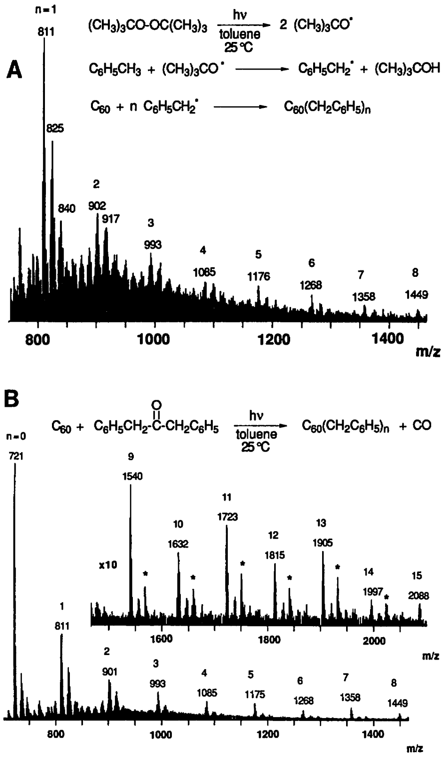


Fig. 3. Fast-atom bombardment (FAB) mass spectra of the products obtained by UV irradiation at 25°C of toluene solutions of (**A**) C_{60} and di-*tert*-butylperoxide and (**B**) C_{60} and dibenzyl ketone, showing the formation of $C_{60}(CH_2C_6H_5)_n$ adducts with n = 1 to 8 (A), and n = 1 to 15 (B). Masses corresponding to adducts with benzyl and methyl groups (for example, 825, 840, and 917 *m/z*) are also seen in (A). In (B), the mass clusters labeled with an asterisk are 28 mass units heavier than the mass of the nearest C_{60} benzyl derivative and correspond to adducts with benzyl groups and one benzylcarbonyl group.

The multiple addition of benzyl radicals to C_{60} is fully supported by fast-atom-bombardment mass spectrometry of the solutions after photolysis (*12*). The mass spectrum of Fig. 3A shows products of addition of one to eight benzyl radicals to C_{60}.

Benzyl radicals can also be generated by alternative routes, for example, by photolysis of dibenzyl ketone. The ESR spectra are essentially indistinguishable from those described above, and the mass spectrum of the solution after photolysis shows the addition of up to 15 benzyl radicals to C_{60} (Fig. 3B). Multiple addition of free radicals to C_{60} is not confined to benzyl radicals. For example, photochemically generated *tert*-butoxy radicals in benzene solutions of C_{60} at elevated temperatures (>50°C) do not add to the latter, nor do they react with the solvent, but instead fragment into acetone and methyl radicals (*13*) that add to C_{60}. In Fig. 4, mass spectrometric analysis of a solution obtained by prolonged photolysis at 100°C of C_{60} and di-*tert*-butylperoxide in benzene shows C_{60} adducts bearing from 1 to at least 34 methyl groups.

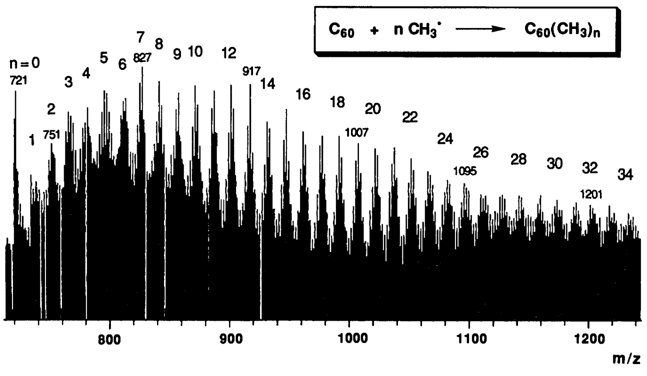


Fig. 4. FAB mass spectra of the products obtained by UV irradiation of a benzene solution of C_{60} and di-*tert*-butylperoxide at 100°C that show the formation of $C_{60}(CH_3)_n$ adducts with n = 1 to 34.

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11. Structures with the unpaired electron at these positions correspond to the canonic resonance forms of a cyclohexadienyl radical.
12. After photolysis of at least 30 min in the ESR cavity, most of the solvent was pumped away. The concentrated, clear brown solutions were submitted for MS analysis. These were carried out with a VG-ZAB-E double-focusing mass spectrometer by using a xenon gas fast-atom-bombardment gun and a *m*-nitrobenzyl alcohol matrix.
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