Trapping of Photoenols from *o*-Tolualdehydes in Gas Matrices. Dependence of Photoenol Formation on the Nature of the Carbonyl Function

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o-Methylbenzaldehyde (**1**) and *o*-methylacetophenone (**2**), matrix-isolated in Ar, N_2, Xe, or carbon monoxide, were irradiated with u.v. light. In contrast to the ketone (**2**) which was unreactive, the benzaldehyde gave a photoenol in all gas matrices. Irradiation of 2,5- or 2,4-dimethylbenzaldehyde (**9**) and (**10**), respectively, also produced photoenols under the above conditions. In propan-2-ol under cryogenic conditions, *o*-methylacetophenone (**2**) can be photoisomerized to an enol, probably the consequence of stabilization of the *Z*-enol by hydrogen bonding. 5,8-Dimethyltetralone (**11**) does not give a photoenol in gas matrices, although it is reported to give one at 77 K in EPA.‡ It is proposed that cage effects in gas matrices can significantly alter rates of internal rotation and are determinants in the production of *E*-enols in this environment. I.r. spectral evidence for photoenols is presented for the first time.

The photochemistry of *o*-methyl-substituted phenyl ketones and aldehydes has been extensively studied and a number of comprehensive reviews on this subject have been published.[1,2] The evidence for transient photoenol formation is substantial and includes u.v. absorption spectra,[3,4] deuterium exchange,[5] oxygenation,[6-8] and trapping experiments with dienophiles.[9-12] It has been established that two distinctly different rotamers, *syn* and *anti*, are important in the photochemistry of these systems.[4]

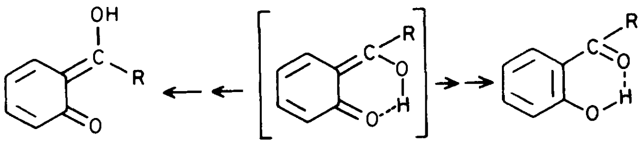
In the preceding paper we report that rotamerization cannot be photoinduced for the related hydroxy analogues, *o*-hydroxyacetophenone (3) and methyl salicylate (4) (which exist as hydrogen-bonded chelates) when they are isolated in gas matrices.[13] However, a new conformational species has been observed when matrix-isolated salicylaldehyde (5) is irradiated with u.v. light. Despite the likelihood of photoinduced hydrogen transfer in this series (3)—(5),[1] no photoenols were observed under cryogenic conditions. Undoubtedly, back hydrogen transfer from intermediate (*A*) to give (ultimately) starting carbonyl species (3)—(5) is faster than internal rotation leading to a unimolecularly stable *E*-enol under these conditions.

By replacing the hydroxy-group of (3) and (5) with methyl, the rate of back hydrogen transfer from OH in excited states should be severely retarded (as hydrogen is now being transferred to carbon) and internal rotation to give *E*-enols may prevail. In the light of the specificity observed for photorotamerization in the series (3)—(5), it is of interest to study the effect of rare-gas matrices on the photoreactivity of (1) and (2); since the formation of *E*-enols requires the rotation of an *exo*-CROH unit, the size of R may be critical.

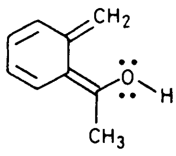
Recently, additional matters for consideration have been raised by Grellman and his co-workers,[14] who have proposed: (1) the existence of two metastable rotamers of the *Z*-enol of *o*-methylacetophenone (**6a** and **b**) with distinct kinetic properties, and (2) a tunnel process, to account for both a large deuterium isotope effect and non-linear Arrhenius plots for the kinetics of reketonization of the *Z*-enol.

The application of i.r. matrix isolation spectroscopy, which is characterized by very high spectral resolution, allows us to analyse for primary photochemical reactions and to relate the spectral characteristics of starting material and photoproducts to specific structural features.

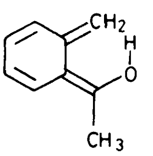
(1) R = H
(2) R = CH_3



E-enol
A
(3) R = CH_3
(4) R = OCH_3
(5) R = H



(6a)



(6b)

Experimental

A description of the apparatus as well as the protocol for preparation of samples has been reported.[15,16] Argon (Matheson; prepurified; 99.998% minimum) was purified according to a procedure described previously. Carbon monoxide, nitrogen, and xenon of research grade purity supplied by Matheson Gas Products were used without further purification.

2,4-Dimethylbenzaldehyde, 2,5-dimethylbenzaldehyde, and *o*-methylacetophenone were supplied by Aldrich Chemical Co., and were purified by g.l.c. 5,8-Dimethyltetralone was synthesized from 4-(2,5-dimethylphenyl)butyric acid using a procedure adapted from that described for α-tetralone.[17-19]

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‡ EPA = diethyl ether–isopentane–ethanol (5 : 5 : 2)

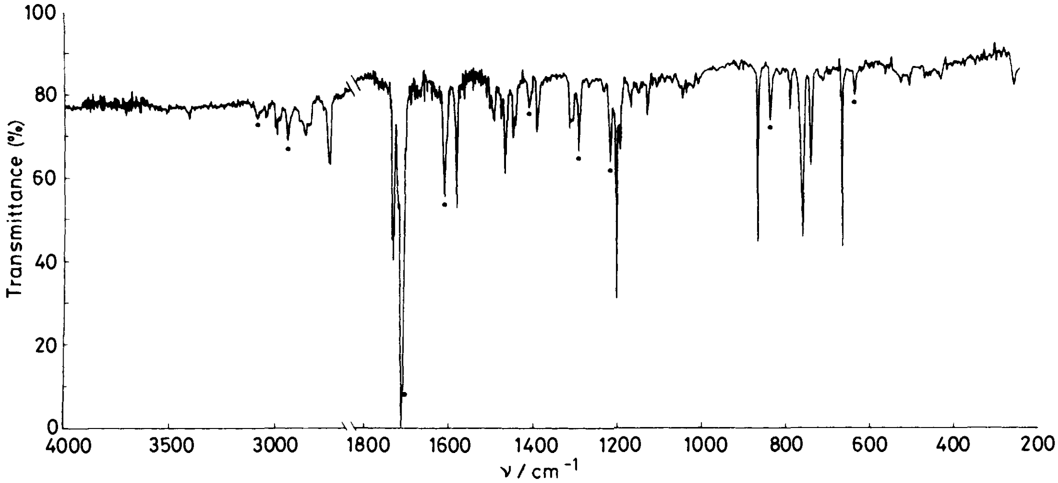


Figure 1. I.r. spectrum of nitrogen-matrix-isolated *o*-methylbenzaldehyde (**1**) (*M*/*R* 550, *T* 12 K, 37 mm). Dots indicate the bands belonging to photochemically less reactive species

Photochemical reactions were carried out with a 1000 W mercury–xenon lamp (Hanovia No. B977B0010). Interference filters (Oriel, No. G-572) were used as indicated.

Results

o-Methylbenzaldehyde (**1**) and *o*-methylacetophenone (**2**) were matrix isolated in argon, nitrogen, carbon monoxide, or xenon, and then irradiated with u.v. light (λ250—350 nm), for periods of 40—70 min, over a temperature range from 12 K to within a few degrees of the softening temperature of the matrix. No major products from the ketone (**2**) were stabilized as the i.r. and u.v. spectra of photolysed (**2**) were similar to those of starting material.

On the other hand, the aldehyde (**1**), which consists of *syn*- and *anti*-conformers of similar thermodynamic stability[4c] (but possesses a barrier to interconversion of *ca.* 30 kJ mol^{-1}), with light of λ 250—300 nm gave a yellowish photoproduct in all the above matrices at 12 K. (At this temperature, in the absence of u.v. light, internal rotation about the C_{sp^2}–CO bond is suppressed.) Our studies show that it is the *syn*-conformer (**1**) whose concentration changes significantly during photolysis. The primary photoproduct (**7**) possesses $\lambda_{max.}$(xenon) 393 nm (Figure 4). Prominent i.r. bands of (**1**) are listed in Table 1. The i.r. spectra of the starting material and photolysate are displayed in Figures 1—3.

The photolysate generated by irradiation of (**1**) with λ 300 nm (Figure 3) also contains a secondary photoproduct (**8**), derived directly from (**7**), that exhibits an O–H stretch (ν 3 553 cm^{-1}; Table 3). Yields of (**8**) can be optimized by irradiating with λ 400 nm. At this wavelength the primary photoproduct (**7**) partitions between (**8**) and (**1**). Benzocyclobutenol is formed in small quantities during the irradiation of (**1**) in solution,[12] and is a logical candidate for (**8**).

Photoproducts (**7**) and (**8**) are stable to the softening temperature of all the aforementioned matrices (*i.e. T* 65 K; Xe). The photoreactivity of (**1**) is matrix-dependent with (**1**) being the least reactive in argon [yellowish colour barely perceptible (*A* 0.08; $\lambda_{max.}$ 390 nm) after irradiation (λ 300 nm) of 15 mm, *M*/*R* 500, for 90 min]. With 40 min irradiation time, (**1**) (15 mm, *M*/*R* 500) reacted in xenon to give (**7**) with an absorbance of *A* 0.30.

In solid carbon monoxide the positions of the i.r. bands of the primary photoproduct are perturbed from values in inert matrices. Most notably the OH stretch is shifted to $\nu_{max.}$ 3 598 cm^{-1}, but this discrepancy is typical for hydrogen-bonded complexes of carbon monoxide with acidic alcohols like phenol.[20b]

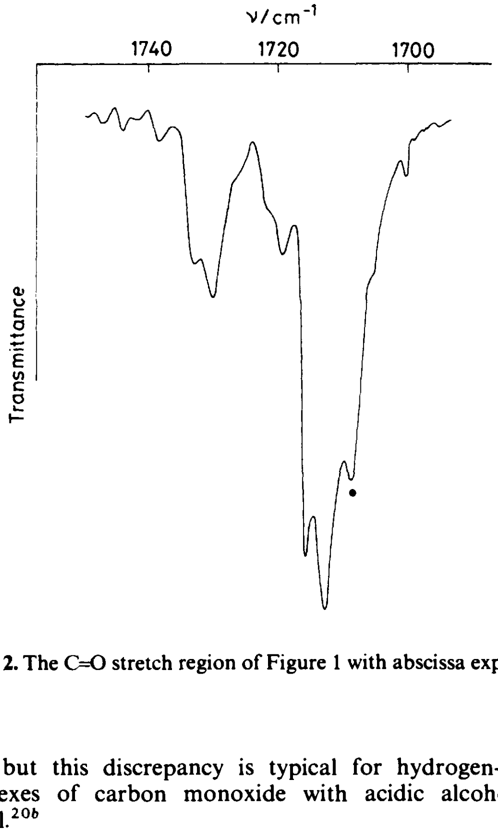


Figure 2. The C=O stretch region of Figure 1 with abscissa expanded 10 times

The photochemical behaviour of 2,5-dimethylbenzaldehyde (**9**) and 2,4-dimethylbenzaldehyde (**10**) parallels that of (**1**) with photoproducts exhibiting $\lambda_{max.}$ in the region of 390 nm in xenon (*M*/*R* 500, 10 K); as in the example of *o*-methylacetophenone (**2**), the conformationally constrained ketone 5,8-dimethyltetralone (**11**) does not give discernible products on irradiation in gas matrices.

Discussion

The photoproduct (**7**) possesses a u.v.–visible spectrum [$\lambda_{max.}$ (xenon) 393 nm] (Figure 4) indicative of an extended chromophore, and is consistent with the properties reported for the photoenol previously derived from (**1**).[3,4,14] I.r. bands (solid

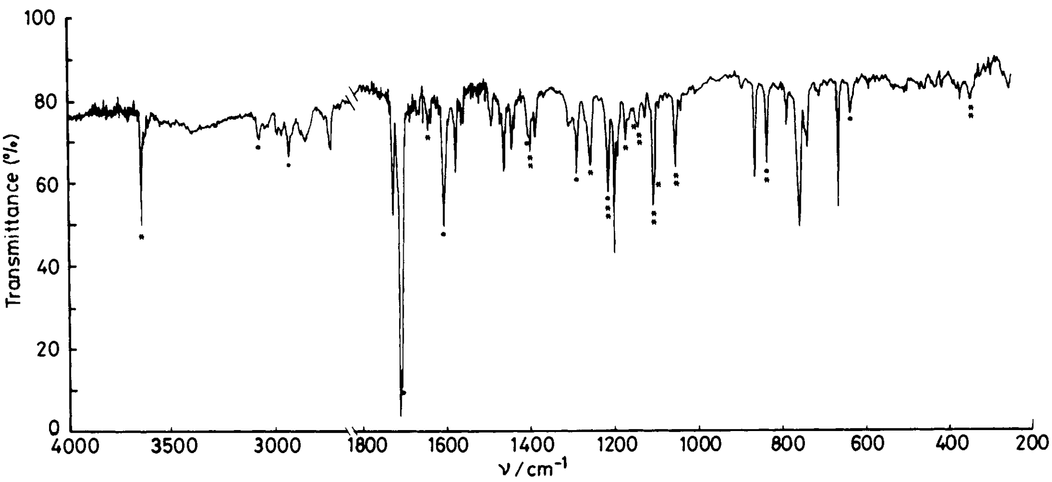


Figure 3. I.r. spectrum of nitrogen matrix-isolated *o*-methylbenzaldehyde (*M*/*R* 500, *T* 12 K, 39 mm) after irradiation for 40 min through a 300 nm interference filter. The bands of primary photoproduct are marked with a single asterisk and of secondary photoproduct with double asterisks. Dots indicate the bands of the photochemically less reactive species

Table 1. Observed vibrational frequencies (cm^{-1}) of nitrogen matrix-isolated *o*-methylbenzaldehyde (**1**)[a,b]

3 080w*	1 580m	1 167w
2 985w	1 490w	1 128w
2 938w*	1 473w	865s
2 852w	1 462m	836m*
2 738m	1 444m	788w
1 733m	1 405w*	759s
1 730m	1 388m	739m
1 715vs	1 308w	664s
1 712vs	1 288m*	634w*
1 708s*	1 212m*	258w
1 609m*	1 201s	

[a] *M*/*R* 550, *T* 12 K, 37 mm. [b] Asterisks indicate the bands of the photochemically less reactive species.

Table 2. Observed vibrational frequencies (cm^{-1}) assigned to the primary photoproduct of nitrogen matrix-isolated *o*-methylbenzaldehyde (**1**)[a]

3 642s	1 147vw
1 646w	1 102m
1 256m	836m[b]
1 172w	

[a] *M*/*R* 500, *T* 12 K, 39 mm. [b] Absorption superimposed on the band observed in starting material.

N_2) at 3 642 (OH str.), 1 646 (C=C str.), 1 256 (OH bend), and 1 102 cm^{-1} (CO str.) support an assignment to a photoenol. That neither (**7**) nor (**1**) upon irradiation at λ 300—400 nm generate species in carbon monoxide with bands typical of free radicals (RCO) (C=O str. *ca.* 1 800—1 900 cm^{-1}) strongly suggests that only isomerizations, rather than fragmentations, are being photoinduced. The photoproduct derived from (**1**) could be either of two geometrical enols, the *Z*-form, *E*-form, or both.

The single sharp resonance characteristic of free OH [ν 3 642 cm^{-1} (Figure 5)] points toward a single photoenol. Circumstantial evidence is derived from the documented kinetic behaviour of *Z*- and *E*-photoenols[1,2,4] obtained from *o*-methylacetophenone. It is well known that the *Z*-enol is considerably less stable to reketonization than is the *E*-form. Based on Grellman's work,[14] the *Z*-enol of (**1**) is expected to be unstable to ketonization at temperatures above 125 K even in protic solvents [assuming kinetic behaviour similar to the *Z*-photoenol (**6**)[4c,14]].

Table 3. Observed vibrational frequencies (cm^{-1}) assigned to the secondary photoproduct of nitrogen-matrix-isolated *o*-methylbenzaldehyde[a]

3 553w	1 212m[b]
3 540w	1 140w
2 938m[b]	1 106m
1 401m	1 055s
1 231w	348w

[a] *M*/*R* 500, *T* 12 K, 39 mm. [b] Absorptions superimposed on the bands observed in starting material.

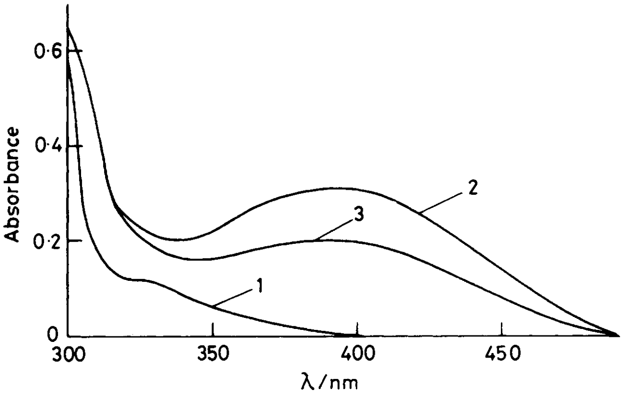
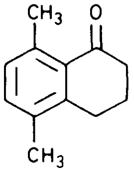
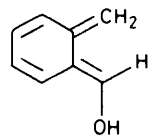


Figure 4. U.v. spectrum of xenon matrix-isolated *o*-methylbenzaldehyde (*M*/*R* 500, *T* 12 K, 15 mm): 1, before irradiation; 2, after irradiation for 40 min, through a 300 nm interference filter; 3, after irradiation through 300 nm (for 40 min) and 400 nm (for 60 min) interference filters

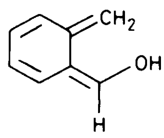
The lifetime of (**6**) is reported to be extremely short at 25 °C in non-polar solvents (< 20 ns in cyclohexane), but is increased in hydrogen-bonding solvents.[4a] The conformationally locked ketone (**13**) is constrained to form a *Z*-enol on irradiation, whose spectral features and kinetics of decay match those of the *Z*-enol (**b**) derived from (**2**). In an EPA glass at 77 K the



(11)



E (7)



Z (12)

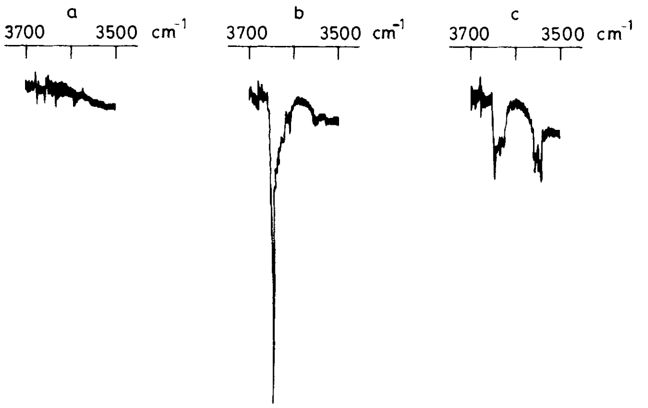
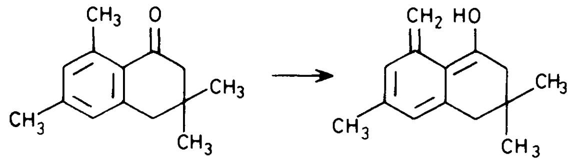


Figure 5. O–H stretch region of the i.r. spectrum of nitrogen matrix-isolated *o*-methylbenzaldehyde (**1**) (*M*/*R* 500, *T* 12 K, 39 mm): a, before irradiation; b, after irradiation for 40 min through 300 mm interference filter; c, after irradiation through 300 nm (for 40 min) and 400 nm (for 60 min) interference filters

photoenol (**14**) is stable for hours, but is reconverted into (**13**) by warming the glass to *ca.* 90 K. By contrast the *E*-enol that is derived from (**2**) possesses a lifetime of 4 s in cyclohexane.

Curiously, our observations using propan-2-ol as a matrix [20a] indicate disparate thermal behaviour for photoenols generated from (**1**) and (**2**) in this solvent at 12 K. Whereas the ketone (**2**) is stable to photoirradiation in rare-gas matrices and nitrogen, a photoenol with absorption at $\lambda_{max.}$ 390 nm is formed from (**2**) in propan-2-ol. Warming of the photolysate to 100 K results in bleaching of the spectrum, which indicates that a product from (**2**) has the stability of a *Z*-enol. In sharp contrast, the photoenol derived from (**1**) is stable to the m.p. of propan-2-ol (180 K). These experiments indicate that the photoenols formed from (**1**) and (**2**) in propanol are geometrically distinct. The thermal stability of the photoenol from (**2**) is consistent with the kinetics of decay reported earlier for the *Z*-photoenols (**6**) and (**14**). Hence, the structure of the photoproduct of (**2**) in propanol is assigned to (**6**). The photoenol derived from (**1**), that is stable to the limit of the matrix (180 K), is likely to be the *E*-enol (**7**).

The evidence is consistent with the notion that *Z*-photoenols may be formed from the ketones (**2**) and (**11**) in gas matrices, but may rapidly revert to starting material perhaps *via* a tunnel reaction. The tetralone (**11**) is configurationally constrained by rigid gas matrices to give only *Z*-enols. That the matrix effect is predominantly steric is suggested by the relatively poor conversion of (**1**) into (**7**) in argon as compared with xenon. We interpret the latter observation as indicating that molecules of (**1**) are tightly surrounded by argon atoms which substantially inhibit their rotational freedom, in both ground and excited states.



(13) (14)

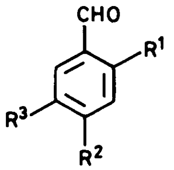
In the accompanying paper we have reported a profound matrix effect in the series salicylaldehyde (**5**), *o*-hydroxy-acetophenone (**3**), and methyl salicylate (**4**) in which only salicylaldehyde can be photorotamerized to the *anti*-form. No photoenols are trapped in this series since the proton-transferred form, in its first excited state, is thought to re-transfer the proton rapidly to the hydroxylic oxygen.

Thus photoenol formation in the tolyl system (**1**) and (**2**) parallels photorotamerization for the hydroxy analogues (**5**) and (**3**). It is the smaller carbonyl function that permits an observable change upon irradiation of the matrix-isolated system. The photochemical behaviour of the dimethyl-substituted benzaldehydes (**9**) and (**10**) parallels that of (**1**) and suggests that photoenol formation may be general for *o*-tolualdehydes under the above conditions.

We must conclude from these studies that the matrix environment exerts a profound effect on the photoreactivity of the isolated species (**1**) and (**2**) owing to cage effects, which are presumably steric in nature. By virtue of imposing conformational constraints on intermediates and starting material, a rigid cage can determine the course of reactions. In i.r. laser studies of nitrous acid, Shirk[21] has demonstrated that the nature of the local environment of the trapped guest is an important determinant for i.r.-laser-induced conformational changes. The rate law for isomerization is adequately accommodated by assuming that energy transfer from excited nitrous acid in unproductive sites is transferred to acceptor molecules in sites which permit internal rotation. Shirk's experiment demonstrates that the orientation of the guest and/or the nature of the local environment can inhibit even modest changes in structure.

Other workers have also observed effects on the photophysics of systems related to (**1**) and (**2**) that may be a consequence of constraints on the rotation of the carbonyl function. Hirota[22] and his co-workers have measured a much slower rate of conversion of fluorescence into phosphorescence during irradiation of salicylaldehyde (**5**), compared with the ketone (**3**), in non-polar solvents at 77 K. They attribute the rate differential to the effect of methyl on rotation of the carbonyl function in the excited state. Migirdicyan *et al.*[3] have noted that over the ranges 160—215 and 215—300 K, the temperature dependence for photoenol formation in durene crystals is the same for 2,5-dimethyl- (**9**), 2,4-dimethyl- (**10**), and 2,4,5-trimethylbenzaldehyde (**15**). This observation is all the more intriguing since the three guest molecules have very different energy gaps between their $^{3}\eta$–Π^{*} and $^{3}\Pi$–Π^{*} states. The data can be interpreted as indicating rate-determining rotation of the carbonyl function (rather than rate-determining hydrogen abstraction) leading to the respective *E*-enols of (**9**), (**10**), and (**15**).

It should also be pointed out that there are a number of instances in which rotamerization involving a carbonyl species occurs in matrices. Conformer ratios of methyl vinyl ketone,[23] aldoketenes,[24] acrolein,[25] and mesityl oxide [20b] can be photochemically and thermally altered at cryogenic temperatures in



(**9**) $R^1 = R^3 = CH_3$, $R^2 = H$
(**10**) $R^1 = R^2 = CH_3$, $R^3 = H$
(**15**) $R^1 = R^2 = R^3 = CH_3$

gas matrices. It is not clear in most instances which groups are actually undergoing large displacements during the rotational process. On the other hand, we have studied systems, *i.e.*, biacetyl[26] and methyl acrylate,[20b] which do not undergo photorotamerization in rare-gas matrices at 20 K.

Application of techniques that give detailed knowledge of the structure of host cage and trapped guest should be the target of future research, in order to provide a basis for rationalizing and predicting the ease of internal rotation which may often be product-determining in matrices.

Acknowledgements

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