Photochemical Behaviour of Matrix-isolated Salicylaldehyde and its Derivatives. Trapping of a Non-hydrogen-bonded Conformer

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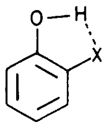
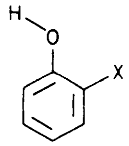
The photochemical behaviour of salicylaldehyde, its 3-, 4-, and 5-methoxy derivatives, 2'-hydroxyacetophenone (7), and methyl salicylate (8) have been investigated in argon, xenon, nitrogen, and carbon monoxide matrices. Non-hydrogen-bonded conformers of salicylaldehyde and methoxysalicylaldehydes were generated using u.v. light ($\lambda_{max.}$ 250 or 300 nm interference filters) and trapped in all matrices that were investigated. New conformers of methyl salicylate (8) and 2'-hydroxyacetophenone (7) are not formed in rare-gas matrices or in solid nitrogen. The data support a model in which the host cage hinders internal rotation of the acetyl and methoxycarbonyl groups of (7) and (8) respectively, in inert gas and nitrogen matrices.

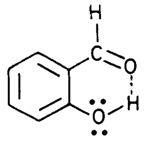
The presence of functional groups containing electronegative atoms in the *ortho*-position of phenols often results in the formation of intramolecular hydrogen bonds.[1] For *ortho*-substituted phenols having intramolecular hydrogen bond energies between 16 and 32 kJ mol^{-1} only the *syn*-isomer (1) has been characterized experimentally.[1,2] Efforts to observed *anti*-conformers (2) have been unsuccessful, primarily because detection of this species by conventional methods requires high temperatures, conditions under which the system is subject to decomposition.[3,4] Thus the spectroscopic properties of *anti*-salicylaldehyde and its derivatives have not been reported. The hydrogen bond strength in such systems has been determined indirectly by means of competing equilibria,[3,4] ultrasonic absorption measurements,[5,6] and correlations between hydroxy proton chemical shifts and torsional frequencies.[7] Theoretical calculations of the hydrogen bond strength of these systems are also available.[8-10]



(1) (*syn*)



(2) (*anti*)



(3)

Salicylaldehyde (3) and its derivatives have also been the target of numerous photophysical and photochemical studies because of their appeal as model systems for intramolecular proton transfer in excited states. Proton transfer in such systems is extraordinarily fast, greater than 10^{11} s^{-1} even at cryogenic temperatures.[11a] The phototautomerism of (3) and related compounds has been extensively studied both experimentally[11,12] and theoretically,[13] and a comprehensive review on this subject has been recently published.[14] *anti*-Conformers (open forms) of salicylaldehyde have been implicated in the time-dependent variation of phosphorescence intensities of photolysed (3) in nonpolar solvents at 77 K and in mixed crystals at 4.2 K.[15,16]

Using the matrix-isolation technique, we now provide *direct* i.r. spectral evidence for the trapping of a non-hydrogen bonded conformer of salicylaldehyde. During the course of this work a profound matrix effect was observed on the photolysis of the corresponding ketone and ester analogues.

Experimental

A description of the apparatus and the preparation of volatile samples has been reported previously.[17,18] Samples with very low vapour pressures were placed in a glass U-tube (located between the cryostat and the needle valve that was used to control the matrix gas flow rate), and were equilibrated at 77 K and then maintained between −15 and 25 °C during deposition. Flow rates of matrix gases (0.2—1.0 mm min^{-1}) were experimentally adjusted in order to obtain sufficient isolation (no detectable dimers) and spectral intensity. The ratio of matrix gas to the sample (*M*/*R*) varied from 200 to 2 000.

Argon (Matheson; prepurified; 99.998% minimum) was purified according to procedures previously described.[17,18] Carbon monoxide, nitrogen, and xenon of research grade purity were supplied by Matheson and were used without further purification. The chemicals utilized in these studies were commercially available and were supplied by Kodak Laboratory and Specialty Chemicals (salicylaldehyde), Fisher Scientific (*o*-cresol), Mallinckrodt (phenol), and by Aldrich Chemical Co. [*o*-^{2}H]Salicylaldehyde was prepared by isotopic exchange with deuteriated water. The purity of samples was established by i.r. spectroscopy and g.l.c.

Photochemical reactions were carried out with a 1 000 W mercury–xenon lamp (Hanova No. B977B0010) as the light source. Interference filters (Oriel, No. G-572 and Zeiss Jena) were used as indicated. Using i.r. spectroscopy to follow the reaction, total irradiation times were generally in the range 15—60 min for 20—30 mm of sample (*M*/*R ca.* 500—600).

Results

Irradiation of argon matrix-isolated (3) leads to the formation of a new species as evidenced by new i.r. bands (Table 1, Figure 2) that grow and disappear at the same rate. The presence of a sharp intense signal in the region of $\nu_{max.}$ 3 638 cm^{-1} is typical of a free (non-hydrogen-bonded) OH stretch[19] and there is evidence for a formyl carbonyl stretch[20] (ν_{CO} 1 708, ν_{CH} 2 882 cm^{-1}) that is shifted to higher frequency from the hydrogen-bonded value of 1 678 cm^{-1}. Of particular interest is the OH

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Table 1. Observed vibrational frequencies (cm^{-1}) of photolysed salicylaldehyde[a,b]

3 638m*	1 391m	922w*
2 882w*	1 342m	886m
2 855w	1 328m	847m*
2 777w*	1 307w*	805w*
2 758w	1 291m	769w
1 708m*	1 281w	759s
1 678s	1 233m	744m
1 654m	1 208m	720m
1 630m	1 189w	669m
1 619m*	1 169w*	632w*
1 608w*	1 152m	562w
1 590m	1 119w	502w*
1 500m	1 096w*	451w
1 468s	1 031w	324m*
1 428w	940w	261w

[a] After irradiation in argon matrix (*M*/*R* 500; *T* 12 K; 26 mm) for 30 min through a 250 mm interference filter (Oriel). [b] The tabulated frequencies were calibrated with polystyrene reference spectrum. Error of reading ±1 cm^{-1}. Asterisks indicate the bands of photoproduct.

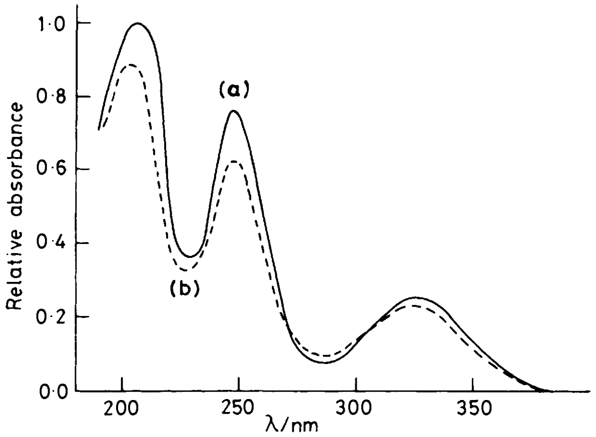


Figure 1. U.v. spectrum of argon matrix-isolated salicylaldehyde (**3**) (*M*/*R* 500; *T* 12 K; 3 mm): (a) before irradiation; (b) after irradiation for 60 min through a 250 nm interference filter (Oriel)

torsion with $\nu_{max.}$ 324 cm^{-1}, which is a normal value for a free hydroxy. The same species is formed from (**3**) with either light of λ 300, 250, or 220 nm, but the photostationary states for the matrix-isolated system differ for each wavelength. I.r. bands for the new species in various environments are listed in Table 2. The u.v.–visible spectrum of photolysed (**3**) (Figure 1) does not differ significantly from that of starting material. This result indicates that there is no major change in electronic structure between salicylaldehyde and the newly trapped species.

The new product is formed in nitrogen, xenon, and carbon monoxide matrices. In solid carbon monoxide, the hydroxy stretch of product ($\nu_{max.}$ 3 564 cm^{-1}) is shifted to lower wavenumbers because of hydrogen bonding to carbon monoxide. This value is reasonable and consistent with the values of carbon monoxide complexes of substituted phenols.[21] Spectral changes that are analogous to those observed for (**3**) are also observed for 2-hydroxy-4-methoxybenzaldehyde (**4**) and 2-hydroxy-5-methoxybenzaldehyde (**5**) when they are irradiated in argon matrices (20—40 min; 20 mm; λ 250 nm). The corresponding photoproduct of 2-hydroxy-3-methoxybenzaldehyde (**6**) differs in some respects. Relevant regions of the spectrum of photolysed (**6**) are shown in Figure 3(a). The

Table 2. Observed i.r. bands (cm^{-1}) of the photoproduct of salicylaldehyde in gas matrices

Matrix i.r. bands Argon	 Nitrogen	 Carbon monoxide
3 638s	3 620s	3 564s
2 882w		
2 777w		
1 708s	1 705s	1 704s
	1 697m	1 696m
		1 640w
1 619s	1 616m	1 616w
1 608m		1 329m
1 307m	1 308m	1 310w
	1 250w	
	1 213m	
	1 178w	
1 169w		
1 096w		
	1 093m	
922w		
847m		848m
	847m	
805m		805m
632w		
502w		508w
	388w	
324s		

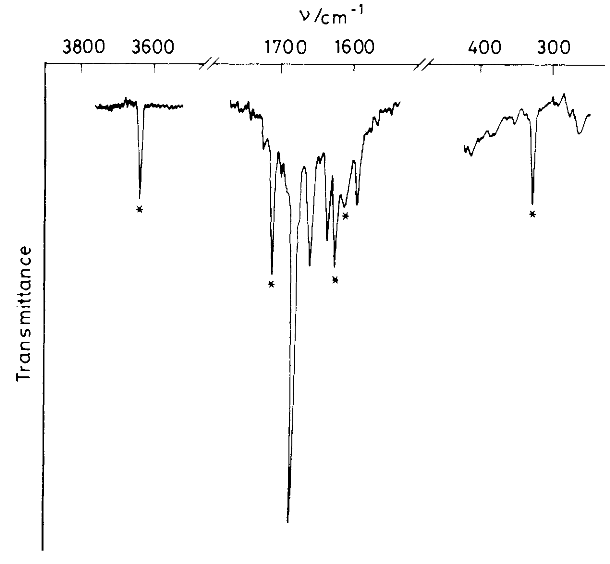
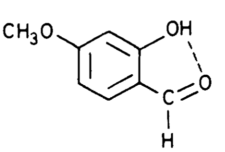
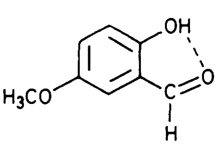
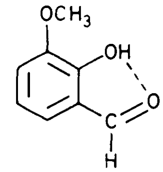


Figure 2. ν_{OH}, $\nu_{C=O}$, and γ_{OH} regions of the i.r. spectrum of argon matrix-isolated salicylaldehyde (*M*/*R* 500; *T* 12 K; 26 mm) after irradation for 30 min through a 250 nm interference filter (Oriel). Asterisks indicate the bands of photoproduct


(**4**)


(**5**)


(**6**)

position of ν_{OH} (3 564 cm^{-1}) and γ_{OH} (450 cm^{-1}) indicate that an intramolecular hydrogen bond has been formed between hydroxy and methoxy groups, thereby demonstrating that an

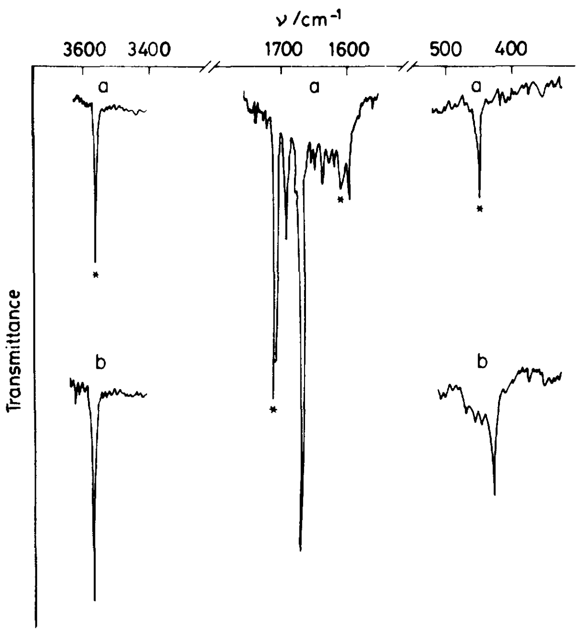
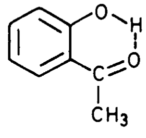
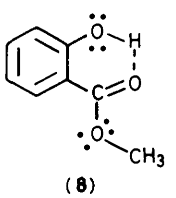


Figure 3. a, ν_{OH}, $\nu_{C=O}$, and γ_{OH} regions of the i.r. spectrum of argon matrix-isolated 2-hydroxy-3-methoxybenzaldehyde (**6**) (*M*/*R* 500; *T* 12 K; 30 mm) after irradiation for 20 min through a 254 nm interference filter (Zeiss Jena). Asterisks indicate the bands of photoproduct. b, ν_{OH} and γ_{OH} regions of the i.r. spectrum of argon matrix-isolated 2-methoxyphenol (*M*/*R* 500; *T* 12 K; 17 mm)



(**7**)



(**8**)

anti-form of OH can be stabilized. Bands at similar frequencies are observed for *o*-methoxyphenol, and for a comparison they are shown in Figure 3(b). Key bands of (**4**)—(**6**) together with absorptions of their photoinduced unchelated forms are compiled in Table 3. Table 3 also includes, from our studies, relevant i.r. data of *o*-substituted phenols in argon matrices as reference points. Thus photoinduced changes are observed for all the benzaldehydes investigated.

However, the photoinduced changes observed with the aldehydes in rare-gas matrices cannot be extended to other carbonyl species, as u.v.-irradiation (λ 220—300 nm; 30—50 min) of related carbonyl analogues such as 2′-hydroxyacetophenone (**7**) and methyl salicylate (**8**) does not lead to new trapped species. [However, 2′-hydroxyacetophenone in solid CO at 12 K upon irradiation (λ 250 nm) forms a new species which exhibits hydrogen bonding to CO, $\nu_{max.}$ 3 562 cm^{-1}].

The photolysate from (**3**) is stable to the softening temperatures of argon, nitrogen, and xenon matrices (65 K). During evaporation of the xenon matrix the lowest temperature at which changes in the i.r. spectrum of the photolysate can be observed and related to starting material is in the region of 120 K.

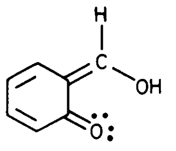
Discussion

Nature of the Photoproduct.—Absorption of u.v. light by (**3**) at cryogenic temperatures could, in principle, result in hydrogen transfer leading to the enols (**9**) and (**10**), and/or the repopulation of the ground state by metastable conformers.

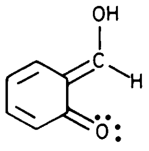
Table 3. Characteristic frequencies (cm^{-1}) of observed conformers in argon matrices at *T* 12 K

Structure	$\nu_{OH/OD}$	$\nu_{C=O}$	$\gamma_{OH/OD}$
(**1**; X = H)	3 634s 3 638s		310s
(**1**; X = NO$_2$)	3 225m^a		750m
(**1**; X = F)	3 616s		371s 364m
(**1**; X = Cl)	3 566s 3 569s		395s
(**1**; X = Br)	3 544s 3 547s		400s
(**1**; X = C≡N)	3 576s 3571sh 3566sh		396m 383m
(**1**; X = OCH$_3$)	3 577s		426m
(**3**)	3 190m^a	1 680vs	720s
[*O*-^{2}H] (**3**)	2 380m^a	1 680vs	520m
(**4**)	*b*	1 665vs	720w
Photolysed (**4**)	3 637m	1 702m	310w 298w
(**5**)	3 215w^a	1 675vs	730m
Photolysed (**5**)	3 642m	1 703m	283w
(**6**)	*b*	1 671vs	725m
Photolysed (**6**)	3 564m	1 712m	450w
(**7**)	*b*	1 650vs	740m
(**8**)	3 188m^a	1 690vs	727m
(**15**)	3 638m	1 708m	324m
[*O*-^{2}H] (**15**)	2 682m	1 708vs	232m
o-Cresol	3 638s		322s 295w 270m

^{a} Broad band. ^{b} Very broad band coalesced with baseline



(**9**)

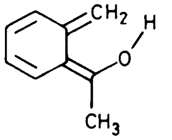


(**10**)

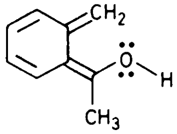
However, it has been extremely difficult to trap photoenols of salicylates and related compounds.[22] In general, pseudo-aromatic rings containing intramolecular hydrogen bonds to a carbonyl show high stability to photolysis despite the relatively small energies (E_a ~ 20—40 kJ mol^{-1}) that are required to break internal hydrogen bonds. The photostability has been accounted for by invoking internal conversion processes that are triggered by proton transfer across the intramolecular hydrogen bond in S_1, with internal conversion taking place from the proton transferred form. In this manner, the photochemically reactive triplet state is effectively bypassed.[23]

Interestingly, an activation energy of 37 kJ mol^{-1} for the formation of 2′-methylacetophenone from ground state *Z*-photoenol in methanol has been reported.[24,25] The effective barriers for the corresponding isomerization of *syn*-photoenols of salicylaldehyde and its analogues are likely to be much smaller, in that hydrogen is transferred between oxygens and quantum-mechanical tunnelling may play a role.[25,26] [Note that it is unclear whether hydrogen bonding of methanol to hydroxy in (**11**) or (**12**) is mainly responsible for the 37 kJ mol^{-1} activation barrier to 2′-methylacetophenone or whether configuration (**12**) (with the hydroxy proton *syn* to methyl), has a significant intrinsic barrier to (**11**).[24,25]]

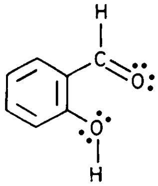
From the i.r. spectrum of photolysate (Table 1, Figure 2) it is clear that the new species retains the functionality that is present



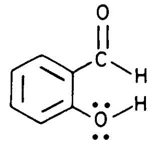
(11)



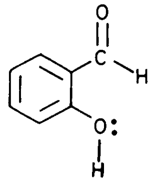
(12)



(13)



(14)

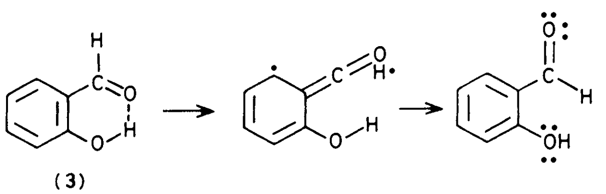


(15)

in starting material with the exception of the internal hydrogen bond. Our failure to observe the absorption of (**9**) or (**10**) in the visible spectrum in the region of 400 nm[15] is evidence against photoenols in the photolysate.[22,27–31]

The most reasonable structure for the new species must be one of the non-hydrogen-bonded conformers (**13**)—(**15**). The i.r. spectral data are entirely consistent with this proposal as 'free' phenolic hydroxyl typically shows an O–H stretch in the region of $\nu_{max.}$ 3 640 cm^{-1} in gas matrices.[19,21a] The out-of-plane bend which is characteristic of strong internal hydrogen bonds in salicylaldehyde analogues (γ_{OH} 720 cm^{-1}) has been displaced to γ_{OH} 324 cm^{-1} which is a normal value for free OH.[1,19] Similarly, the carbonyl stretch of salicylaldehyde has been displaced to $\nu_{max.}$ 1 708 from 1 678 cm^{-1}. The corresponding values for [O-^{2}H]salicylaldehyde and its photoproduct (Table 3) also support an assignment to a conformer. Failure to achieve conformational change in the ester and ketone in Ar, Xe, and N_2 focuses attention on some intrinsic property of the formyl group.

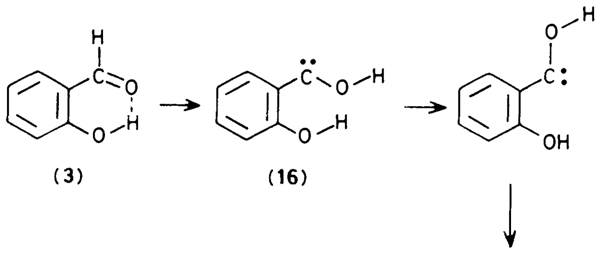
Mechanistic Considerations.—In principle, conformation changes could occur by a novel mechanism involving cleavage of the formyl C–H bond of (**3**) followed by recombination of radicals.



(3)

Hydrogen atoms can be efficiently trapped in carbon monoxide to give formyl radicals[32] which are easily detected. Since absorption at 2 488, 1 861, and 1 090 cm^{-1}, indicative of the formyl radical, is not detected during the photoirradiation of (**3**) in carbon monoxide, we can eliminate the radical pathway from consideration.[32] A path involving oxacarbene formation[33] would also seem untenable because the carbene should be subject to trapping with CO, and the resulting ketenes would be detectable. At any rate, a rotation or inversion of the intermediary carbene (**16**) would still be required to reach (**14**) or (**15**).

Non-hydrogen-bonded conformers of salicylaldehyde (and its carbonyl analogues) can be achieved by rotation of the hydroxy group, and/or by rotation of the more spatially demanding carbonyl function around the aromatic carbon atom to which it is linked. Little is known, however, of the impediments to rotation of organic functional groups in gas matrices, or about the preferred mode (inversion or rotation) to conformational change in such an environment. In contrast to pathways involving bond cleavage, or inversion of configuration, there is ample precedent for the production at cryogenic temperatures of metastable conformers *via* light-induced internal rotation. A growing number of investigators[34–41] have induced changes in conformer ratios at low temperature by photoirradiation.



(3) (16)

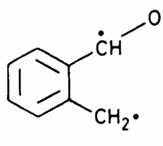
(3b or c)

Our experience with quenching *o*-halogenophenols and *o*-cyanophenol from the gas phase (298 K) in which both *syn*- and *anti*-levels are populated suggests that non-hydrogen-bonded conformers can rapidly revert to hydrogen-bonded species even at cryogenic temperatures. These phenols show only a hydrogen-bonded conformer when condensed from the gas-phase onto a plate cooled to 20 K; nor have we been able to trap the *anti*-forms by excitation with u.v. light.[21a] (Barriers to rotation for *anti*-forms of *o*-halogenophenols lie between 12 and 17 kJ mol^{-1}.[42]) Failure to observe both phenolic conformers is especially striking, insofar as we have been able to stabilize both conformers in other two-component systems such as methyl vinyl ketone that are separated by barriers of *ca.* 8—13 kJ mol^{-1}.[43]

To explain this distinction between $\alpha\beta$-unsaturated carbonyl systems and *o*-halogenophenols at least two additional factors need to be considered besides the distribution of conformers undergoing internal conversion from the excited state. First, quenching of high-temperature equilibria between these *ortho*-substituted phenolic conformers may not be feasible because of quantum-mechanical tunnelling which is known in phenolic systems.[26] Second, internal rotation of the vinyl or carbonyl moieties of acrolein and related $\alpha\beta$-unsaturated carbonyls has greater steric requirements than does internal rotation or inversion of the hydroxy function in *o*-halogenophenols. Therefore, in gas matrices it may be easier to preserve a non-Boltzian distribution of conformers that is generated photochemically, in the case of $\alpha\beta$-unsaturated carbonyl systems, as opposed to *o*-halogenophenols.

That the determinants for photorotamerization of matrix-isolated species are subtle is evident from Shirk's i.r.-laser studies of nitrous acid.[44] Analysis of the kinetic data indicates that extensive energy migration occurs in solid nitrogen and argon, and reactive molecules form only a small subset of the total guest molecules. Apparently the reaction occurs at sites where the isomerization is least hindered by the cage. Thus, Shirk's experiments demonstrate that the orientation of the guest and/or the nature of the local environment can inhibit even modest changes in structure.

Of the three planar conformations lacking a hydrogen bond, we favour a structure in which the formyl group has rotated 180° from (**3**); (**13**) in which the carbonyl has not rotated seems the least likely photoproduct. Of the conformers (**14**) and (**15**), the latter would appear to be the more stable, and is the most attractive alternative because non-bonded repulsions between hydrogens of formyl and hydroxy are minimized. The barrier to rotation of the formyl group in (**15**) is probably in the range of



(17)

24—42 kJ mol^{-1} and this value is consistent with the thermal stability of our photoproduct.[45] We have been able to induce rotation of a formyl group using u.v. light in a number of rare-gas matrix-isolated systems including acrolein, 2-chlorobenzaldehyde, or pyrrole-2-carbaldehyde as guests, so this process has precedents.[21a] On the other hand, we have been unable to trap non-hydrogen-bonded conformers of *o*-halogenophenols in which the hydroxy has rotated, despite significant rotational barriers of 12—17 kJ mol^{-1} between open and hydrogen-bonded forms.

If stable conformers at cryogenic temperatures could be achieved simply by inverting or rotating hydroxy, the ketone (**7**) and ester (**8**) with intrinsic barriers similar to the aldehyde (**3**) for these processes should also give new conformers in rare-gas matrices upon excitation. Strong circumstantial evidence that rotation of the formyl group must occur to give rise to a new species is derived from our studies of 2-methylbenzaldehyde[14] and 2'-methylacetophenone.[15] Only the aldehyde can be photoinduced to form an *E*-enol analogous to (**10**) in argon, nitrogen, and xenon matrices, the ease of formation occurring in that order. These observations are consistent with the notion of steric constraints on rotation of the carbonyl function in rare-gas matrices and nitrogen, with formyl in (**3**), and CHOH in (**17**) being functions capable of rotation in this series.

Acknowledgements

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